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W. Kuczynski [a] [b] , K. Bergmann [a] & H. Stegemeyer [a]

[a] Department of Physical Chemistry, University of Paderborn, D-4790, Paderborn, F. R. Germany

[b] Institute of Molecular Physics, Polish Academy of Science, Poznań

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A MODEL OF THE BLUE PHASE OF CHOLESTERYL ESTERS

W. KUCZYNSKI*, K. BERGMANN, and H. STEGEMEYER
Department of Physical Chemistry, University of
Paderborn, D-4790 Paderborn, F. R. Germany

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Abstract: A model of the so-called Blue Phase of cholesterogenic liquid crystalline systems is proposed with the molecular axes inclined to the helix axis by a critical angle of 54.74°. This model results in a spherical refraction indicatrix compatible with the lack of birefringence as well as with the cholesteric-like optical properties.

In several preceding papers[1-4] we have reported that some optical properties of the two different polymorphic Blue Phases (BP) of cholesteryl esters and other cholesterogenic systems characterized by small helical pitches are quite similar to that of the corresponding cholesteric state. The BP exhibits (i) anomalous optical rotatory dispersion (ORD), (ii) selective reflection (SR) of circularly polarized light of the same sense as in the cholesteric state, (iii) angular dependence of SR following the same Bragg-like relation as known for cholesterics,[5] and (iv) Cano lines in a wedge-shaped sample[6] as found in cholesterics.[7]

These results led us to the conclusion that the two different Blue Phases (BP I and BP II) we observed[2-4] are at least nothing but thermodynamically stable varieties of the well-known cholesteric state. On the other hand, cholesteric and BP state show a significant difference in optical double refraction: cholesteric phases are (negatively) birefringent ($\Delta n < 0$) whereas BP are not ($\Delta n = 0$).[1,8] It should be mentioned that for the high temperature BP II the lack of birefringence is not entirely valid up to date because of its very small temperature range of existence.

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[*] On leave of absence from the Institute of Molecular Physics, Polish Academy of Science, Poznań.

Whereas ORD and SR results indicate an anisotropic helical molecular arrangement in the BP state[1] the lack of birefringence on the other hand has been discussed to be the result of a random distribution of helical axes.[9] Different tilt directions of helical axes with respect to the incident light, however, would lead to a considerable broadening of the SR bands[5] which have been scanned by transmission measurements.[3] Therefore, the assumption of globular screw-like structured assemblies[9] is not compatible with our experimental results of very sharp SR bands.[3] The same seems to be due to the cubic lattice model proposed by Saupe.[10] The aim of this letter is to explain this seeming contradiction in optical properties by a simple model of molecular orientation within the BP state.

According to the model of de Vries[5] in cholesteric phases the average direction of the molecular long axes always is perpendicular to the helix axis leading to an oblate refraction indicatrix ($\Delta n < 0$) with an optical axis parallel to the helix axis. In compensated cholesteric mixtures with nematic properties the indicatrix turns to a prolate one ($\Delta n > 0$).[11] The question arises if any molecular arrangement is possible leading to a spherical indicatrix ($\Delta n = 0$) with optical isotropy but preserving the helical structure. It can be easily shown that the negative indicatrix of cholesterics changes to a positive one if the tilt angle Θ of the local director against the helical axis decreases from 90° to zero.

According to the model of de Vries in cholesterics the local director lies perpendicularly to the helical axis ($\Theta = 90°$). As the local optical symmetry is approximately uniaxial the principal values n_1 and n_2 of the refractive index parallel and perpendicular to the local optical axis are related to the experimental indices of the ordinary and extraordinary rays n_o and n_e, respectively, by

$$n_o = [\frac{1}{2}(n_1{}^2 + n_2{}^2)]^{1/2} \qquad (1)$$

$$n_e = n_2. \qquad (2)$$

The de Vries model of cholesterics[5] can be extended by introduction of a variable tilt angle Θ between the local director and the helical axis. If Θ decreases ($\Theta < 90°$) it can be derived from Fig. 1 that eqs. (1) and (2) change to

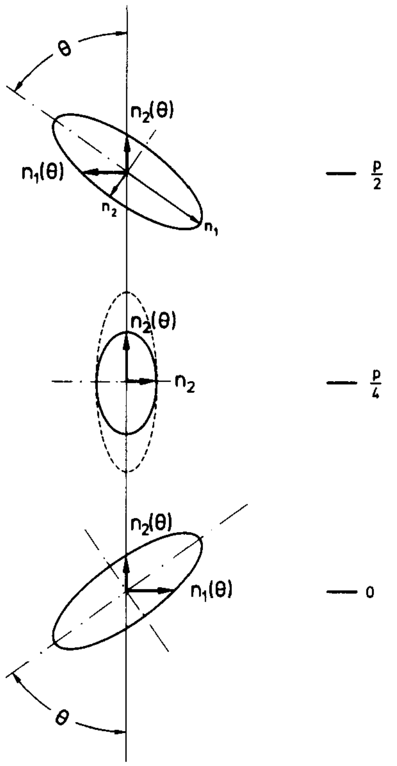

Figure 1

Influence of the tilt angle Θ between the helical axis and the local refraction indices n_1 (Θ) and n_2 (Θ). n_1, n_2: principal values of the refraction indices parallel and perpendicular to the director; P: helical pitch

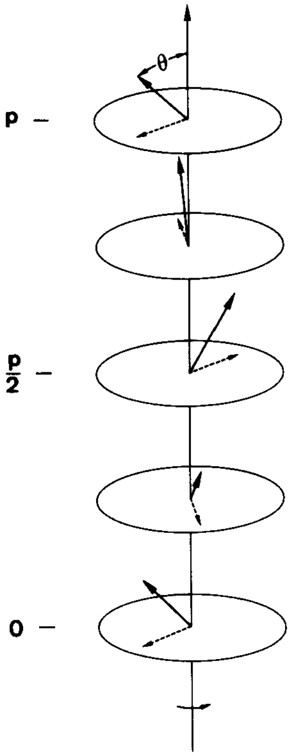

Figure 2

Tilted helical structure for the BP resulting in a spherical indicatrix. P: helical pitch; Θ: tilt angle

$$n_o = [\frac{1}{2}(n_1{}^2(\Theta) + n_2{}^2)]^{1/2} \qquad (3)$$

$$n_e = n_2(\Theta) \qquad (4)$$

where $n_1(\Theta)$ and $n_2(\Theta)$ denote the effective local refractive indices.

For the local rotational elipsoid it follows that

$$n_1{}^2(\Theta) = n_1{}^2 \cdot \sin^2\Theta + n_2{}^2 \cdot \sin^2\Theta \qquad (5)$$

$$n_2{}^2(\Theta) = n_1{}^2 \cdot \cos^2\Theta + n_2{}^2 \cdot \sin^2\Theta. \qquad (6)$$

The birefringence $\Delta n = n_e - n_o$ can be calculated from eqs. (3) and (4) by means of eqs. (5) and (6) considering the relation $\sin^2\Theta = 1 - \cos^2\Theta$:

$$\Delta n = [\frac{1}{2}(n_1{}^2 - n_2{}^2)(3\cos^2\Theta - 1)]^{1/2}. \qquad (7)$$

According to eq. (7) the double refraction vanishes if

$$3\cos^2\Theta_c - 1 = 0. \qquad (8)$$

Eq. (8) is satisfied for a critical tilt angle

$$\Theta_c = 54.74°.$$

Thus, the birefringence of a helically arranged assemble of molecules vanishes if their long axes are tilted against the helical axis by an angle of 54.74°. This value of Θ_c also has been derived by Schröder[12] from a molecular statistical treatment of the cholesteric phase. Because of the limited accuracy of refraction measurements by means of an Abbé refractometer a very small birefringence of the order of $\Delta n < 10^{-3}$ cannot be excluded. In the case of cholesteryl esters it follows from eq. (8) that the tilt angle Θ_c only can be given with an uncertainty of ± 2°.

It should be emphasized that the BP model of a tilted cholesteric structure (Fig. 2) is in agreement with all known experimental results though no physical reason can be given until now why the tilt angle should assume the critical value Θ_c close below the clearing point. There may possibly exist other molecular arrangements which also account for zero double refraction without removal of a uniaxial helical structure in the BP state.

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