Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

On the anomalous temperature dependence of ferroelectric S_{c^*} liquid crystals

Masahiro Nakagawa[a]
[a] Department of Electrical Engineering, Faculty of Engineering, The Technological University of Nagaoka, Nagaoka, Niigata, Japan

To cite this Article Nakagawa, Masahiro(1988) 'On the anomalous temperature dependence of ferroelectric S_{c^*} liquid crystals', Liquid Crystals, 3: 5, 573 — 582
To link to this Article: DOI: 10.1080/02678298808086402
URL: http://dx.doi.org/10.1080/02678298808086402

Liquid Crystals, 1988, Vol. 3, No. 5, 573–582

On the anomalous temperature dependence of ferroelectric S_{C^*} liquid crystals

by MASAHIRO NAKAGAWA

Department of Electrical Engineering, Faculty of Engineering, The Technological University of Nagaoka, Kamitomioka 1603-1, Nagaoka, Niigata 940-21, Japan

(*Received 25 September 1987; accepted 30 December 1987*)

A biaxial elastic model for the temperature dependence of S_{C^*} helical pitch is proposed on the basis of a phenomenological theory of S_{C^*} liquid crystals accompanied by a biaxial molecular ordering playing an important role for the anomalous behaviour of the helical pitch near the S_{C^*}–S_A transition point. In the S_{C^*} phase of *p*-(*n*-decyloxybenzylidene)-*p*-amino-(2-methylbuthyl)-cinnamate (DOBAMBC), a qualitative agreement with the observed helical pitch is found by choosing a few material parameters concerned with a biaxial elasticity and an anisotropy of the elastic constants.

1. Introduction

In most ferroelectric S_{C^*} liquid crystals, a fascinating temperature dependence of the S_{C^*} helical pitch has been observed [1–3]. First a weak temperature dependence of the S_{C^*} helical pitch is found relatively far from the S_{C^*}–S_A transition points. As a whole the S_{C^*} helical pitch slowly increases with increasing temperature. Next an anomalous temperature dependence of the helical pitch, i.e. a steeply decreasing helical pitch towards the S_{C^*}–S_A transition point, is also observed in the temperature range $T_c - T < 1$ (K); here T_c denotes the Curie temperature [2], Kondo *et al.* studied the temperature dependence of the helical pitches for *n*OBAMBC homologous in the vicinity of the S_{C^*}–S_A transition points by means of a laser diffraction method [2]. Later, by the same method, Blinc *et al.* worked out a detailed measurement on the temperature dependence of the DOBAMBC helical pitch [3]. Their observations explored that in the immediate vicinity of T_c the S_{C^*} helical pitches for the homologous series tend to decrease abruptly as if they were going to vanish completely at the Curie points. However, they confirmed that the helical pitches did not vanish completely at the S_{C^*}–S_A transition points but remained to be certain finite values. In addition Kondo *et al.* observed such anomalous behaviour of the helical pitch in the S_{C^*} sample with a cell thickness of more than $100\,\mu$m in which any anchoring effect may be neglected [2].

To explain theoretically the above-mentioned anomalous behaviour of the helical pitch, some different approaches have been so far proposed [4–6, 15]. First Osipov and Pikin put forward a qualitative explanation for the anomalous flexoelectric coefficient from a molecular theoretical aspect [5]. As far as we are aware, however, no quantitative comparison with an experimental result has been reported up to date. Next from a phenomenological aspect, Yamashita and Kimura [4] investigated the effect of the critical director fluctuation on the temperature dependence of the S_{C^*} helical pitch based on the Landau theory originated by Pikin and Indenbom [8]. They concluded that a considerably large thermal fluctuation of the tilt angle near the S_{C^*}–S_A

transition point may increase the number of turns of the helicoidal structure and result in such anomalous behaviour of the S_{C*} helical pitch, and that the helical pitch completely vanishes at the S_{C*}–S_A transition point proportional to the square of the molecular tilt angle [4]. In accord with their conclusion, however, the critical fluctuation effect takes no account of the anomalous behaviour for such a large monodomain size confirmed experimentally with a sufficiently thick sample [2]. Apparently this conclusion contradicts the experimental finding that the anomalous behaviour is independent of a sample thickness of more than about $100\,\mu$m [2]. In fact, as was noted later by Musevic *et al.* [18], the critical director fluctuation considered by Yamashita and Kimura [4] cannot result in the experimentally observed anomalous temperature dependence of the helical pitch.

Alternatively Blinc *et al.* tried to explain such anomalous behaviour including a non-chiral biquadratic coupling term between the molecular tilt and the polarization as well as an anharmonic term into the conventional Landau free energy derived by Pikin and Indenbom [1, 3, 7, 8, 19]. In their approach, the non-chiral biquadratic term is considered to be related with a bipolar ordering about the long molecular axis, and plays an important role for the anomalous behaviour of the S_{C*} helical pitch [3]. Moreover, although a qualitative agreement with the experimental S_{C*} helical pitch was found, they could not explain why the large contribution of the biquadratic coupling term between the molecular tilt and the spontaneous polarization was required.

Analogously, Huang and Dumrongrattana [6] also proposed a generalized mean-field model for the S_{C*}–S_A transition similar to that proposed by Zeks [7]. They found good agreement with the experimental data by choosing a number of adjustable parameters for DOBAMBC. Like Blinc *et al.* [3], they also considered that the anharmonic chiral term plays an important role in the slow variation of the S_{C*} helical pitch far from the S_{C*}–S_A transition point. Their approaches suggested that the bipolar ordering might be significant for the anomalous behaviour of the helical pitch. Such a bipolar ordering about the long molecular axis may be strongly coupled to a biaxial ordering in S_{C*} phases. As is well known for the S_C phase, the biaxial order results in the biaxiality of the refractive indices more than the bipolar one [9]. This may be also the case for the S_{C*} phase since the difference in thermodynamic properties between chiral DOBAMBC as S_{C*} and a racemic mixture as S_C is found to be negligibly small [3, 18]. Moreover, as was reported by Straley [18], such biaxiality may exist even in nematic and S_A phases, which are usually supposed to be uniaxial since the biaxial order is very small. In fact, as is experimentally confirmed by Blinc *et al.* [3, 19], there exists a bipolar ordering about the long molecular axes in the S_{C*} phase. The orders of the biaxial and the bipolar orderings are found to be comparable in S_C phases [9]. Consequently, the free energy expression in the S_{C*} phase has to be extended to include a possible biaxiality. From these aspects, it seems to be significant to introduce a biaxiality into the S_{C*} free energy originated by Pikin and Indenbom and its modified versions [6–8, 11].

As will be explored in this work, such a biaxial elastic feature becomes dominant in the elastic free energy in the immediate vicinity of the S_{C*}–S_A transition point because both twist and bend elastic energies in the S_{C*} helicoidal structure become rather small compared with the biaxial elastic energy, and therefore have no role in the behaviour of the helical pitch near the transition point. From a similar aspect, Goossens pointed out that the anomalous behaviour of the S_{C*} helical pitch may result from such a possible molecular biaxiality in the vicinity of the Curie point [15]. In his conclusion, however, the helical pitch vanishes proportional to the square of the tilt angle in contradiction with the experimental observations [1-3].

Several different models for the anomalous temperature dependence of the S_{C^*} helical pitch have been proposed by many workers to date, but the situation has still to be clarified as mentioned above. The purpose of the present paper is to show the relation between such anomalous behaviour and the molecular biaxial ordering which is not included in the nematic-like free energy of S_{C^*} liquid crystals formulated by Lagerwall and Dahl [11]. In addition we will explore the significance of the anisotropy of the elastic constant as well as the biaxial ordering on the temperature dependence of the S_{C^*} helical pitch. To clarify the role of the biaxiality in this work, we shall ignore the biquadratic coupling studied by Blinc *et al.* for simplicity [3]. From a numerical evaluation, for DOBAMBC liquid crystals, one may find a qualitative agreement with the experimental helical pitch [3] for a relatively wide temperature range by choosing a few parameters as the anisotropy of the elastic constants and the biaxial order parameter. In §2 we shall outline in brief a generalized free energy expression based on the Landau–de Gennes theory for the biaxial nematics. Then a numerical estimation for the anisotropy of the elastic constants and the biaxial order parameter is given in §3, in comparison with the experimental helical pitch for DOBAMBC by Blinc et al. [3] Finally §4 provides a few concluding remarks on the present model.

2. Theory

According to Lagerwall and Dahl [11], the free energy density $f_{S_{C^*}}$ for the ferroelectric S_{C^*} state free from any layer dilatation and distortion can be written as

$$\begin{aligned} f_{S_{C^*}} = {} & \frac{\alpha}{2} e^2 + \frac{\beta}{4} e^4 + \frac{K_1}{2} (\nabla . n)^2 \\ & + \frac{K_2}{2} (n . \nabla \times n + q_T)^2 + \frac{K_3}{2} (n \times \nabla \times n)^2 \\ & + \frac{\mathbf{P}_s^2}{2\chi} + \mu_p \mathbf{P}_s . \mathbf{e} - \mu_f \mathbf{P}_s . (n \times \nabla \times n), \end{aligned} \tag{1}$$

where the first and the second terms in the right-hand side correspond to an energy density concerned with the molecular tilt in the unwound S_C state, α and β are appropriate constants, n is the local director along the average direction of the long molecular axes, K_1, K_2 and K_3 are the splay, twist and bend elastic constants, respectively, q_T is the inherent twist wave number arising from the molecular chirality, χ is the dielectric susceptibility, μ_p and μ_f are the piezo- and the flexoelectric constants, respectively, P_s is the spontaneous polarization vector, and e is a vector order parameter defined by

$$e = (n \times v)(n . v), \tag{2}$$

where v is the layer normal unit vector. The nematic-like expression equation (1) is equivalent to a more general expression derived by Dahl and Lagerwall [21] when no layer distortion or dilatation exists. In the free energy $f_{S_{C^*}}$, the twist energy proportional to $K_2 q_T n . \nabla \times n$ is involved. In the S_{C^*} phase, however, banana-like S_{C^*} molecules may possess a biaxial ordering about the long molecular axis as was noted in the previous section [9, 10, 15]. In addition, as was pointed out by Straley [10], such a biaxial ordering may exist even in nematic (N) or S_A phases. Of course, in such a case, there may exist a helicoidal structure even in S_A phase as was pointed out by Pikin and Indenbom [8]. Therefore such a biaxial effect has to be included in the free energy expression. Before introducing the biaxial molecular ordering into the free energy $f_{S_{C^*}}$, it may be convenient to consider first the Landau–de Gennes free energy for uniaxial cholesterics [22] in terms of the following uniaxial tensor order parameter:

$$Q_{ij} = \tfrac{3}{2}S(n_i n_j - \delta_{ij}/3). \tag{3}$$

Here S is the orientational order parameter of the long molecular axes about the local director n and leads to 1 for a saturated molecular orientation. Using such a symmetric and traceless tensor order parameter Q_{ij}, the free energy density may be written as

$$f_{S_{C^*}} = \frac{\alpha}{2}e^2 + \frac{\beta}{4}e^4 + \frac{L_1^0}{2}Q_{ij,k}Q_{ij,k} + \frac{L_2^0}{2}Q_{ij,i}Q_{kj,k} - 2L_1^0 q_T \varepsilon_{ijk} Q_{il} Q_{jl,k} + \frac{\mathbf{P}_s^2}{2\chi} + \mu_p P_{s_i} e_i + \mu_f P_{s_i} Q_{ji,j}, \tag{4}$$

where L_1^0 and L_2^0 are also the elastic constants related to K_1, K_2 and K_3, by $K_2 = 9L_1^0 S^2/2$, $K_1 = K_3 = 9(2L_1^0 + L_2^0)S^2/4$ [14], ε_{ijk} is the Levi–Civita tensor, and the repeated indices follow the Einstein convention. The second elastic constant L_2^0 stands for the anisotropy of the elastic constants. If $L_2^0 = 0$, then of course there exists no anisotropy of the elastic constants for splay, twist and bend deformations, or $K_1 = K_2 = K_3$. For most nematics, $L_2^0 > 0$ or $K_2 < K_1 \simeq K_3$ is usually observed. As was experimentally confirmed by Rosenblatt *et al.* [20], the condition $K_1 \simeq K_3$ is almost satisfied for DOBAMBC. If one needs to remove the degeneracy between K_1 and K_3, the third-order terms in Q_{ij} has to be included as was pointed out by Schiele and Trimper [24]. Such a refined approach will be reported in the near future together with some experimental results. At this stage we ourselves shall resort to the second-order form expressed by equation (4), which may reasonably be accepted for DOBAMBC as was noted above. In a biaxial phase such as S_{C^*} we have to introduce the following biaxial tensor order parameter instead of the uniaxial one or equation (3):

$$Q_{ij} = \tfrac{3}{2}S(n_i n_j - \delta_{ij}/3) + \frac{b}{2}(m_i m_j - p_i p_j), \tag{5}$$

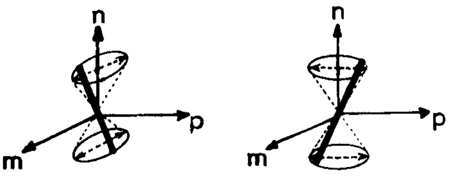
where the unit vectors m and p are defined by

$$m = p \times n, \tag{6}$$

and

$$p = (v \times n)/|v \times n|, \tag{7}$$

respectively. In equation (5), b stands for a biaxial molecular ordering transverse to the long molecular axes [9, 11, 23]. If the molecular orientation is biased along $m(p)$, then $b > 0$ (<0) as is shown in figure 1. Although both order parameters, S and b, can be determined on the basis of a molecular aspect, it is beyond the scope of the present work. In the biaxial state such as the S_{C^*} phase, the tensor order parameter Q_{ij} in equation (4) should be replaced by the biaxial one expressed by equation (5) as was noted by Govers and Vertogen [23] for biaxial nematics. Substituting equation (5)



(a) b>0 (b) b<0

Figure 1. An explanation for the biaxial order parameter b. Here n is the longitudinal director along the average orientation of the long molecular axes, m and p are the transverse directors perpendicular to n. A S_{C^*} molecule is modelled into the bold bar. (*a*) and (*b*) are for $b > 0$ and $b < 0$, respectively.

into equation (4), we can discuss the biaxial S_{C^*} phase in a phenomenological manner. First minimizing $f_{S_{C^*}}$ with respect to P_s, we can derive

$$P_{s_i} = -(\mu_p e_i + \mu_f Q_{ji,j}). \tag{8}$$

Then the minimized free energy $f_{S_{C^*}}$ is given by

$$\begin{aligned} f_{S_{C^*}} = {} & \frac{\alpha'}{2}\mathrm{e}^2 + \frac{\beta}{4}\mathrm{e}^4 + \frac{L_1^0}{2} Q_{ij,k}Q_{ij,k} + \frac{L_2'}{2} Q_{ij,i}Q_{kj,k} \\ & - 2L_1^0 q_{\mathrm{T}} \varepsilon_{ijk} Q_{il} Q_{jl,k} - L_2' q_{\mathrm{B}}' e_i Q_{ji,j}, \end{aligned} \tag{9}$$

where $\alpha' = \alpha - \chi\mu_p^2$, $L_2' = L_2^0 - \chi\mu_f^2$, and the bend wave number q_{B}' is defined by $\chi\mu_f\mu_p/L_2'$.

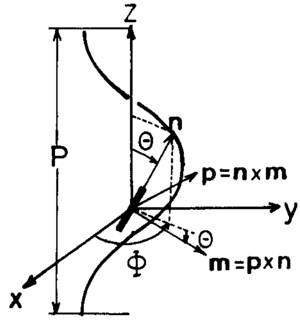


Figure 2. The helical structure along the z axis coincident with the layer normal direction. P denotes the helical pitch. Θ and Φ are the tilt and the azimuthal angles, respectively.

Now we shall hereafter restrict our interest to a uniformly wound helicoidal structure with the helical axis along the z axis in the laboratory frame as is depicted in figure 2. In such a case, the unit vectors n, m and p are simply expressed by

$$n = (\eta\cos qz,\ \eta\sin qz,\ \xi), \tag{10a}$$

$$m = (\xi\cos qz,\ \xi\sin qz,\ -\eta), \tag{10b}$$

$$p = (-\sin qz,\ \cos qz,\ 0), \tag{10c}$$

respectively; here $\eta = \sin\Theta$, $\xi = \cos\Theta$ and $q = 2\pi/P$ is the wave number of the helicoidal structure with a helical pitch P(see figure 2). In this case, the non-vanishing components of $Q_{ij,k}$, $Q_{ij,z}$ are given by

$$Q_{ij,z} = \tfrac{3}{2}S\eta q(p_i n_j + n_i p_j) + \frac{b}{2}\xi q(p_i m_j + m_i p_j) + \frac{b}{2} q(c_i p_j + p_i c_j) \tag{11}$$

where c is the so-called c director defined by

$$c = (\cos qz, \sin qz, 0). \tag{12}$$

Then substituting equation (11) into equation (9), after a straightforward calculation, we can readily obtain

$$f_{\mathrm{S_{C^*}}} = \frac{\alpha'}{2}\eta^2\xi^2 + \frac{\beta}{3}\eta^4\xi^4 + \frac{L_1}{2}\eta^2 q^2 + \frac{L_2}{2}\eta^2\xi^2 q^2 + \frac{L_\mathrm{B}}{2}\xi^2 q^2$$
$$- L_1\eta^2 q q_\mathrm{T} + L_2\eta^2\xi^2 q q_\mathrm{B} - L_\mathrm{B}\xi^2 q q_\mathrm{T}, \tag{13}$$

where L_1, L_2, L_B are q_B are defined by

$$L_1 = \frac{L_1^0}{2}(3S + b)^2 \simeq \tfrac{9}{2}L_1^0 S^2, \tag{14a}$$

$$L_2 = \frac{L_2'}{4}(3S - b)^2 \simeq \tfrac{9}{4}L_2' S^2, \tag{14b}$$

$$L_\mathrm{B} = 2L_1^0 b^2, \tag{15}$$

and

$$q_\mathrm{B} = 2q_\mathrm{B}'/(3S - b), \tag{16}$$

respectively. Here L_1 and L_2 are an isotropic and an anisotropic components of the elastic constants, respectively [14]. L_B is an elastic constant proportional to the square of the biaxial order b and may play an important role for the stabilization of the helical structure near a $\mathrm{S_{C^*}}$–$\mathrm{S_A}$ transition point. Indeed, if b is assumed to have a finite value near the Curie point, the elastic energy concerned with L_B may become dominant because of the factor ξ^2 and result in the anomalous temperature dependence of the $\mathrm{S_{C^*}}$ helical pitch. In equation (13), expanding the above free energy in terms of the tilt angle Θ, we can easily derive the coefficients of the harmonic and the anharmonic terms, proportional to $\Theta^2 q$ and $\Theta^4 q$ as $-(L_1 q_\mathrm{T} - L_2 q_\mathrm{B})$ and $(L_1 q_\mathrm{T} - 4L_2 q_\mathrm{B})/3$, respectively. From this result it should be noted here that the harmonic and the anharmonic terms may have the same sign, as was assumed in the previous works [3, 6–8], if $L_2 q_\mathrm{B} < L_1 q_\mathrm{T} < 4L_2 q_\mathrm{B}$ or $4L_2 q_\mathrm{B} < L_1 q_\mathrm{T} < L_2 q_\mathrm{B}$. According to the experimental fact that the polar order parameter of the transverse dipoles is very small, of the order of 0·1–0·01 [12], the biaxial ordering is also weak [9]. Therefore such a transverse twist energy concerned with L_B seems to be much smaller than the longitudinal twist energy concerned with L_1 and L_2 far from the $\mathrm{S_{C^*}}$–$\mathrm{S_A}$ transition point. In the vicinity of the $\mathrm{S_{C^*}}$–$\mathrm{S_A}$ transition point, however, since the tilt angle becomes very small and the longitudinal twist energy has a tendency to vanish with the increasing temperature, such a transverse twist energy becomes rather dominant in the total elastic free energy than the longitudinal one if b remains to be finite at the Curie point. Now minimizing equation (13) with respect to q, one can readily obtain

$$q = \frac{L_1\eta^2 q_\mathrm{T} - L_2\eta^2\xi^2 q_\mathrm{B} + L_\mathrm{B}\xi^2 q_\mathrm{T}}{L_1\eta^2 + L_2\eta^2\xi^2 + L_\mathrm{B}\xi^2}, \tag{17}$$

From this expression we may expect that the helical pitch shows a temperature dependence through the temperature dependence of the tilt angle Θ. Then eliminating q from equation (13), the minimized free energy can be expressed in terms of η and ξ as

$$f_{S_{C^*}} = \frac{\alpha'}{2}\eta^2\xi^2 + \frac{\beta}{4}\eta^4\xi^4 - \frac{1}{2}\frac{(L_1\eta^2 q_T - L_2\eta^2\xi^2 q_B + L_B\xi^2 q_T)^2}{L_1\eta^2 + L_2\eta^2\xi^2 + L_B\xi^2}. \tag{18}$$

Finally minimizing the free energy with respect to Θ, one can determine numerically the temperature dependence of the molecular tilt angle. Then substituting the value of Θ into equation (17), we can evaluate the temperature dependence of the helical pitch. In the next section, a numerically evaluated result for DOBAMBC will be provided and compared with the experimental data by Blinc *et al.* [3].

3. Numerical results

In this section, let us compare the numerical results with the experimental [3]. From equation (17), the helical pitch P can be written as

$$\frac{P}{P_0} = \frac{L_T}{\Lambda_T}, \tag{19}$$

where $P_0 = 2\pi/q_T$, L_T and Λ_T are defined by

$$L_T = \eta^2 + \lambda_2\eta^2\xi^2 + \lambda_B\xi^2, \tag{20}$$

and

$$\Lambda_T = \eta^2 - \lambda_2\kappa\eta^2\xi^2 + \lambda_B\xi^2, \tag{21}$$

respectively, and the parameters, λ_2, λ_B and κ are defined by

$$\lambda_2 = L_2/L_1, \tag{22a}$$

$$\lambda_B = L_B/L_1, \tag{22b}$$

$$\kappa = q_B/q_T, \tag{22c}$$

respectively, which are to be determined in comparison with experimental observation of the helical pitch. Here, of course, we may expect the relation $\lambda_B \ll 1$ as a consequence of a weak biaxial ordering as was previously noted [9]. Moreover from the above expression, we may predict that the helical pitches for $\eta = 0$ are the same as that for $\eta = 1$ or the cholesteric state. Next in a more familiar form, we can rewrite approximately the minimized free energy expressed by equation (18) as follows:

$$\begin{aligned} f_{S_{C^*}} &= \frac{\alpha'}{2}\Theta^2 + \frac{\beta'}{4}\Theta^4 + O(\Theta^6) - \frac{L_1}{2}q_T^2\frac{\Lambda_T^2}{L_T}, \\ &\simeq \frac{\alpha'}{2}\Theta^2 + \frac{\beta'}{4}\Theta^4 - \frac{L_1}{2}q_T^2\frac{\Lambda_T^2}{L_T}, \end{aligned} \tag{23}$$

where β' is a constant related to both α and β, and experimentally evaluated [13]. In the mean field approximation, α' can be assumed to be

$$\alpha' = \alpha^0(T^* - 1), \tag{24}$$

where $T^* = T/T_c$. From the experimental data for DOBAMBC, Carlsson and Dahl [13] evaluated as $\alpha^0 = 1{\cdot}84 \times 10^7\,\mathrm{J/m^3}$, $\beta' = 8{\cdot}5 \times 10^5\,\mathrm{J/m^3}$ and $L_1 q_T^2/2 \simeq 1$. P_0 can

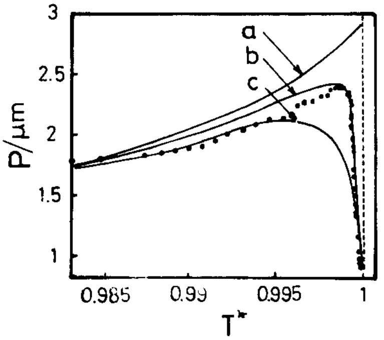


Figure 3. Comparison between the theoretical and the experimental results. P and T^* are the helical pitch and the reduced temperature, respectively. Solid circles give the experimental data for DOBAMBC obtained by Blinc *et al.* Here $\lambda_2 = 0{\cdot}115$ and $\kappa = 5{\cdot}7$. Curves *a*, *b* and *c* are for $\lambda_B = 0$, $0{\cdot}0025$ and $0{\cdot}01$, respectively.

be evaluated as $0{\cdot}89\,\mu$m from P at $T = T_c$ [3]. Making use of the above-mentioned parameters and equations (19)–(21) and (23), one can determine the temperature dependence of the S_{C^*} helical pitch for certain values of λ_2, κ and λ_B. In figure 3, let us present a numerical result as an example together with the experimental helical pitch measured by Blinc *et al.* [3]. From this result, the importance of the biaxial elastic contribution to the free energy may be understood. As was previously noted, in order to estimate the biaxial order and its temperature dependence in S_{C^*} and S_A phases, we have to resort to a molecular theory of S_{C^*} liquid crystals. However, this problem has not been solved as yet and is beyond the scope of the present work. A qualitative explanation for the presence of biaxial ordering will be given in the next section. At this stage we assume constant values of S and b from the following. For the DOBAMBC sample studied by Blinc *et al.* [3], a qualitative agreement was numerically found for $\lambda_2 = 0{\cdot}115$, $\kappa = 5{\cdot}7$ and $\lambda_B = 0{\cdot}0025$ as shown in figure 3. Here the relation $\lambda_B \ll 1$ seems to reflect well the fact that the biaxial order parameter b is smaller than the uniaxial one of S. Assuming that $S \gg b$ and $S \simeq 1$, we can evaluate $|b| \simeq 0{\cdot}08$ from equation (22 *b*). The sign of b may be expected to be negative according to the experimental observations for S_C liquid crystals [9]. This is considered as a result that the director fluctuation may be more easily induced along p rather than m because the latter fluctuation may be accompanied by the smectic layer dilation as was pointed out by Galerne [9]. One may conclude that DOBAMBC liquid crystals possess a positive anisotropy of the elastic constants or $\lambda_2 \simeq L_2'/(2L_1^0) \simeq (K_3 - K_2)/K_2 > 0$. From $\kappa = q_B/q_T \simeq 2\chi\mu_p\mu_f/(3q_T) > 0$, one may expect that $\mu_p\mu_f > 0$ for DOBAMBC because $q_T > 0$. This conclusion is just consistent with the experimental findings by Ostrovskii *et al.* [12]. In addition the present result implies that while such an anisotropy of the elastic constants is very small, the effect of it becomes important to explain the slowly varying S_{C^*} helical pitch in the region of $T^* < 0{\cdot}998$ as shown in figure 3. This conclusion is just reminiscent of that of Goossens who also concluded that the difference $K_3 - K_2 > 0$ between the bend and the twist elastic constants is significant in explaining the moderate temperature dependence in agreement with the present result [15]. In our estimation, the ratio of the twist chiral term $L_1 q_T$ to the bend chiral term $L_2 q_B$ may be evaluated as $1/(\lambda_2\kappa) \simeq 1{\cdot}5$. Therefore the competition between the twist and the bend elastic energy results in a moderate temperature dependence far from the S_{C^*}–S_A transition point, consistent with Goossens [15]. Next, in our model, the biaxial molecular ordering is found to be closely related to the anomalous behaviour in the vicinity of the S_{C^*}–S_A transition point. This conclusion again corresponds to that of Goossens [15]. He also concluded that the biaxial ordering at the S_{C^*}–S_A transition point results in the anomalous change of the helical pitch. In his conclusion, however, P vanishes at the transition point proportional to Θ^2 which is inconsistent with the experimental findings [1–3]. To conclude this section, in our model the anisotropy of the elastic constants and the biaxial ordering play important roles in the slowly increasing and then steeply decreasing helical pitch with increasing temperature, respectively. Apparently such anisotropy of the elastic constants was not involved in the approach proposed by Blinc *et al.* [3]. In the next section, we shall give a few concluding remarks on the present model.

4. Concluding remarks

We have given a simple description of the anomalous temperature dependence of the S_{C^*} helical pitch. Taking account of the biaxial molecular order about the local director in the elastic free energy, we examined the temperature dependence of the S_{C^*} helical pitch. In our conclusion, both the anisotropy of the elastic constants and the biaxial ordering seem to be significant in explaining such an anomalous temperature dependence of the S_{C^*} helical pitch. In particular it is interesting to see that both the bipolar ordering studied by Blinc *et al.* [3] and the biaxial ordering introduced here result in similar anomalous behaviour. As was noted by Straley [10], the bipolar and the biaxial molecular orderings should be strongly coupled to each other. Therefore these two effects seem to contribute more or less to the anomalous phenomena. From a numerical estimation, we found a qualitative agreement between the theoretical temperature dependence and the experimental one for DOBAMBC liquid crystals by Blinc *et al.* [3], and confirmed that the transverse twist elastic constant L_B may be much smaller than the longitudinal twist elastic constant L_l by about an order of 3. In addition, we could estimate the biaxial order parameter b as $-0{\cdot}08$ for DOBAMBC. From our result, it may be expected that the critical value of the helical pitch with $\Theta \simeq 0$ may be almost the same as with $\Theta \simeq \pi/2$, and that the temperature corresponding to a maximum helical pitch tends to be lowered for the S_{C^*} phase with a large biaxial order. This prediction has been experimentally confirmed by us for 4-decyloxybenzylidene-4′-amino-1*p*″-methylpropylcinnamate (DOBA-1-MPC) and will be reported in the near future together with a somewhat refined model related to the present work.

To conclude, we have to mention the physical origin of the biaxial ordering. To our knowledge, there exist a few possible origins for such a biaxial ordering. In S_C phases [9] there exists the anisotropy of the thermal fluctuations of the director which induces the biaxial order. In addition the molecular alignment is monoclinic and the free rotation about the long molecular axes may be biased, giving rise to biaxiality. In the S_A phase with $\Theta = 0$, there cannot exist the above-mentioned origins concerned with the tilted alignment. Nevertheless the biaxiality of the molecular shape of S_{C^*} liquid crystals may give rise to a biased rotation around the long molecular axes as was pointed out by Straley [10] and Freiser [16] for biaxial nematics. In their conclusions, with an appropriate biaxiality of the molecular interaction, the biaxial state becomes more stable than the uniaxial one. Therefore it is plausible there exists a biaxial molecular ordering, which as was noted by Goossens [15] may be small, not only in the S_{C^*} phase but also in S_A. The biaxiality in the S_A phase of a S_{C^*} liquid crystal results in a helicoidal structure for the transverse director *m* or *p* instead of the longitudinal one *n*. In fact it is possible for this type of S_A phase to exist as was pointed out by Pikin and Indenbom [8]. Therefore, in our model, the S_{C^*}–S_A transition is classified as a structural transition between subgroups C_2 and D_2 instead of the conventional one between C_2 and D_∞. From an experimental point of view, since the optical anisotropy is very small, it seems to be difficult to observe the biaxial helicoidal structure in the S_A phase by using an optical microscope. It may be possible to detect such a biaxiality in the S_A phase of S_{C^*} liquid crystals by measuring carefully the optical dispersion of the transmittance for the normally incident light in a homeotropically aligned cell. In addition, it is also considered to be important to evaluate the microscopic order parameters *S* and *b* on the basis of a molecular theory of S_{C^*}. Considering a biaxial interaction between molecules [17] the biaxial twisting power may be derived in a molecular theoretical manner. These problems remain to be investigated in the future.

The author would like to thank Professor T. Akahane for his invaluable discussions and continuous encouragement throughout the present work.

References

[1] Blinc, R., and Zekst, B., 1978, *Phys. Rev. A*, **18**, 740.
[2] Kondo, K., Takezoe, H., Fukuda, A., and Kuze, E., 1982, *Jnp. J. appl. Phys.*, **21**, 224.
[3] Blinc, R., Zeks, B., Musevic, I., and Levstik, A., 1984, *Molsc. Crystals. liq. Crystals.*, **114**, 189.
[4] Yamashita, M., and Kimura, H., 1982, *J. phys. Soc. Japan*, **51**, 2419.
[5] Osipov, M. A., and Pikin, S. A., 1982, *Zh. éksp. teor. Fiz.*, **82**, 774.
[6] Huang, C. C., and Dumrongrattana, S., 1987, *Phys. Rev.*, **A34**, 5020.
[7] Zeks, B., 1984, *Molec. Crystals liq. Crystals*, **114**, 259.
[8] Pikin, S. A., and Indenbom, V. L., 1978, *Sov. Phys. Usp.*, **21**, 487.
[9] Galerne, Y., 1978, *J. Phys., Paris*, **39**, 1311. Photinos, D. J., and Bos, P. J., 1979, *Phys. Rev.*, **A20**, 2203. Lockhart, T. E., Gelerinter, E., and Neubert, M. E., 1982, *Phys. Rev.*, **A25**, 2262.
[10] Straley, J. P., 1974, *Phys. Rev.*, **A10**, 1881.
[11] Lagerwall, S. T., and Dahl, I., 1984, *Molec. Crystals liq. Crystals*, **114**, 151.
[12] Ostrovskii, B. I., Rabinovich, A. Z., Sonin, A. S., and Strukov, O. A., 1978, *Sov. Phys. JETP*, **47**, 912.
[13] Carlsson, T., and Dahl, I., 1983, *Molec. Crystals. liq. Crystals*, **95**, 373.
[14] Sheng, P., and Priestly, E. B., 1975, *Introduction to Liquid Crystals*, edited by E. B. Priestly, P. J. Wojyowicz, and P. Sheng, (Plenum Press), chap. 10.
[15] Goossens, W. J. A., 1986, *Liq. Crystals.*, **1**, 521.
[16] Freiser, M. J., 1970, *Phys. Rev. Lett.*, **24**, 1041; 1971, *Molec. Crystals. liq. Crystals*, **14**, 165.
[17] Nakagawa, M., 1988, *Liq. Crystals*, **3**, 63.
[18] Musevic, I., Zeks, B., Blinc, R., Jansen, L., Seppen, A., and Wyder, P., *Ferroelectrics*, **58**, 51.
[19] Blinc, R., Vilfan, M., and Seliger, J., 1983, *Bull. magn. Reson.*, **5**, 51.
[20] Rosenblatt, C., Pindak, R., Clark, N. A., and Meyer, R. B., 1979, *Phys. Rev. Lett.*, **42**, 1220.
[21] Dahl, I., and Lagerwall, S. T., 1984, *Ferroelectrics*, **58**, 215.
[22] Berremann, D. W., and Meiboom, S., 1984, *Phys. Rev.*, **A30** 1955.
[23] Govers, E., and Vertogen, G., 1984, *Phys. Rev.*, **A30**, 1998.
[24] Schiele, K., and Trimper, S., 1983, *Phys. Stat. Sol. (b)*, **118**, 267.