Invited Lecture. Helical twisting in cholesteric mesophases: Molecular structure and microscopic description

L. N. Lisetski[a]; A. V. Tolmachev[a]

[a] All-Union Single Crystals Scientific Research Institute, Kharkov, U.S.S.R.

PLEASE SCROLL DOWN FOR ARTICLE

Invited Lecture

Helical twisting in cholesteric mesophases: molecular structure and microscopic description

by L. N. LISETSKI and A. V. TOLMACHEV

All-Union Single Crystals Scientific Research Institute, Kharkov, U.S.S.R.

Recent studies of cholesteric systems are briefly reviewed, with special attention paid to the relationship between the molecular structure of the optically active molecules and the helical twisting features. Microscopic models are presented which provide an account of specific intermolecular interactions, conformational equilibria, etc. Mechanisms of dopant-induced helix distortions are discussed based on N.M.R. studies. The use of cholesteric systems as solvents for selective reflection spectroscopy is considered.

1. Introduction

The provision of an adequate microscopic description of cholesteric mesophases formed by chiral molecules of differing chemical structure has been one of the most challenging problems in the field of liquid crystal science [1]. In fact, rigorous molecular statistical theories of cholesterics [2–5] definitively fail to account for essentially different helical twisting features produced by subtle changes in molecular structure. On the other hand, a semi-phenomenological approach based on the quasi-nematic layer concept [6–10] seems to provide a realistic insight into the nature of cholesteric twist. This approach has been further developed [11–15] to describe helical twist in cholesteric systems with different natures, such as cholesterol esters, nematic–cholesteric mixtures and nematics with optically active dopants. These results are summarized in a review [1]. The present article is, in fact, its direct sequel and continuation, with the aim of summing up some of the most recent studies in the field of model description of molecular structure and helical twist in cholesterics.

In the past two or three years there has been a certain shift in the focus of interest in the field of cholesterics from purely physical models and approaches to those taking advantages of physico-chemical concepts. In §2 of this paper we discuss the thermodynamics of intermolecular association in multicomponent cholesteric systems, their effect upon the helical twist and the possibilities of using cholesteric solvents as a tool for studying specific intermolecular interactions. Section 3 deals with conformational changes of the molecular structure leading to helical pitch anomalies, and in §4 we present some new data concerning chiral dopants of high molecular asymmetry in a nematic.

2. Helical twist and specific intermolecular interactions: quasi-binary nematic systems in cholesteric solvents

It is well known that the properties of nematics comprising components of different chemical classes can be strongly influenced by specific intermolecular

interactions. In these systems the nematic–isotropic transition temperature, the elastic constants, the dielectric anisotropy, etc., vary, as a rule, non-linearly with concentration and in some cases even exhibit extrema [16, 17]. Specific interactions are very strong, e.g. in nematic mixtures with induced smectic phases [18, 19] or in mixtures of nematics and cholesterol esters with their helical twist anomalies [1, 12, 20]. However, there have only been a few thermodynamics studies of intermolecular interactions in the mesophase (e.g. estimates of the entropy and enthalpy values for the cyanobiphenyl dimer formation [21] and association in the nematic–cholesteric mixtures [22]).

Let us consider a cyanobiphenyl–Schiff's base system (e.g. 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA)). In this system the following particles can be present: cyanobiphenyl molecules (C), MBBA molecules (M), cyanobiphenyl dimers (C$_2$), and mixed dimers (CM). The association process

$$C + M \rightleftarrows CM$$

is characterized by the enthalpy, ΔH_a, and entropy, ΔS_a, and the dimerization process
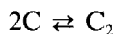
$$2C \rightleftarrows C_2$$

by ΔH_d and ΔS_d. If the molar concentrations of the components are x_c and x_m and the actual concentrations of particles of each kind are c_i, then we may write

$$K_a = \frac{c_{CM}}{c_C c_M}, \tag{1}$$

$$K_d = \frac{c_{C_2}}{c_C^2}, \tag{2}$$

$$c_{CM} + c_M = x_M, \tag{3}$$

$$2c_{C_2} + c_{CM} + c_C = x_C, \tag{4}$$

where K_a and K_d are association and dimerization constants, respectively. Using the relationships

$$\ln K_a = -\frac{\Delta H_a}{RT} + \frac{\Delta S_a}{R}, \tag{5}$$

$$\ln K_d = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R}, \tag{6}$$

we can, by solving equations (1)–(4), obtain model temperature dependences of c_i. With ΔH_d and ΔS_d values taken from [21] (where they had been determined from experimental data for cyanobiphenyls using the Kirkwood–Froehlich equation), and estimating $\Delta H_a/\Delta S_a$ from the thermal stability of the induced low temperature phase [23], these model dependences are shown in figure 1. It appears that for quite realistic parameter values there can be a temperature region within the mesomorphic range of the mixed system where the degree of cyanobiphenyl dimerization increases with temperature (and does not decrease, as for pure cyanobiphenyls).

In an attempt to find a macroscopic effect in which this feature could be manifested, we have used the MBBA–5CB pair as the nematic component of a nematic–cholesteric
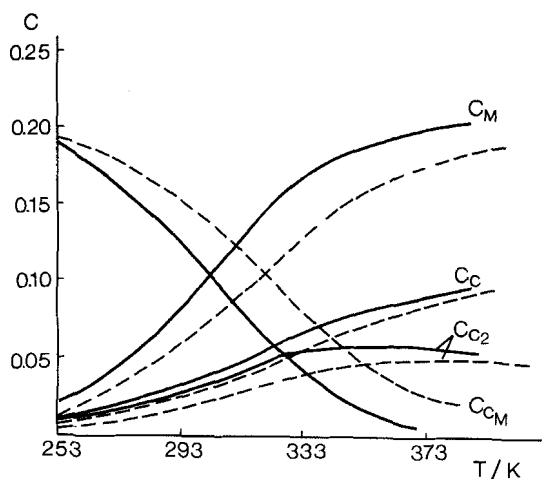
Figure 1. Model dependence of dimer and monomer concentration on temperature in the cyanobiphenyl–Schiff's base system. In these calculations ΔH (kJ mol^{-1}) and ΔS (J mol^{-1} K^{-1}) were for the dimer $-16{\cdot}7$ and $-28{\cdot}4$ and for the mixed dimer -60 and -170 (solid lines) as well as -50 and -130 (broken line), respectively.

mixture. As for the cholesteric component, we have used, as in [24], a mixture of 80 per cent cholesteryl oleate and 20 per cent cholesteryl chloride (CO/CC). The wavelength of maximum reflection λ_{max} values ($\lambda_{max} = np$, where p is the helical pitch and n is the refraction index) for MBBA + CO/CC and 5CB + CO/CC mixtures are shown in figure 2. We note that the non-linearity of p^{-1} versus concentration is much more pronounced for the systems with MBBA (see figure 3), which can be explained
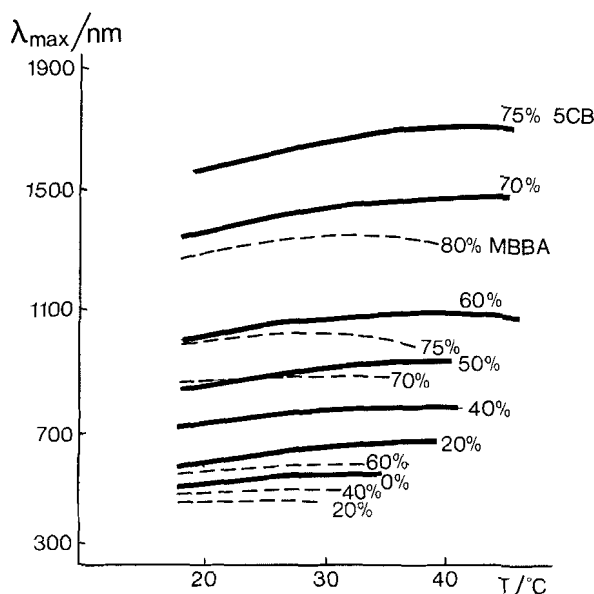

Figure 2. Pitch–temperature dependences in nematic–cholesteric mixtures of 5CB + CO/CC (solid lines) and MBBA + CO/CC (broken lines). Maximum selective reflection wavelength $\lambda_{max} = np$.
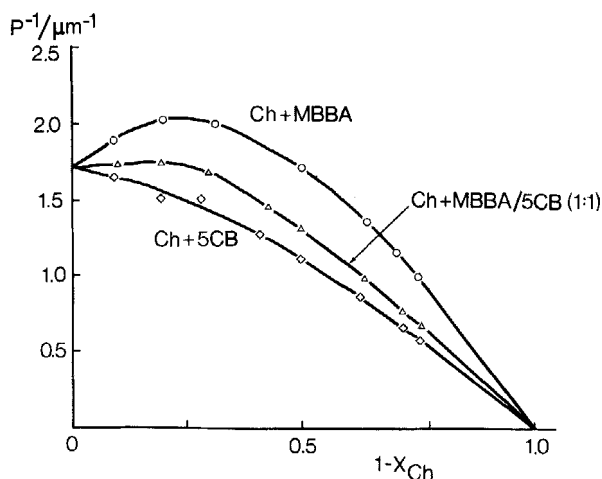
Figure 3. Inverse pitch–concentration dependences in nematic–cholesteric mixtures at 32°C.

by the dimer formation in 5CB reducing the effect of specific steric repulsions [12]. This implies that the helical pitch should be sensitive to changes in the degree of cyanobiphenyl dimerization.

λ_{max} (T) dependences for the MBBA/5CB (1:1) + CO/CC system for different concentrations of the cholesteric component are given in figure 4. In the region of higher temperatures there is nothing unusual; p^{-1} is close to additivity (see figure 3, curve 3). At lower temperatures, however, there is a marked anomaly; the helical pitch increases sharply in a narrow temperature range, which is presumably due to dissociation of the mixed dimer and an increase in the cyanobiphenyl dimer concentration. This type of pitch–temperature dependence is quite unusual and can hardly
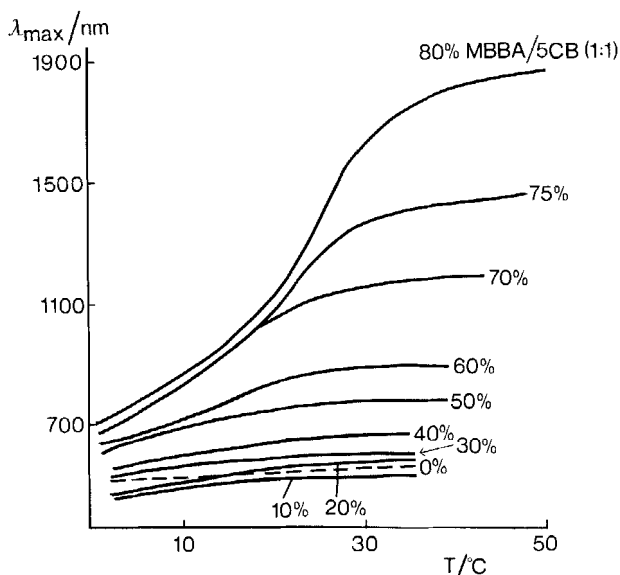

Figure 4. Temperature dependences of helical pitch in nematic–cholesteric mixtures of 5CB/MBBA (1:1) + CO/CC.

be explained by existing theoretical models which do not take into account specific interactions and intermolecular association processes.

The observed increase of p in the range 10–30°C corresponds to an increase of the cyanobiphenyl dimer concentation in the same temperature region (see figure 1). The value of the enthalpy for the mixed dimer formation ($\Delta H_a \approx 65\,kJ\,mol^{-1}$), obtained from the model parameter fitting, seems to be a reasonable estimate, with the mixed dimers being much more stable than the cyanobiphenyl dimer ($\Delta H_d \approx 16\,kJ\,mol^{-1}$ [21]).

Thus, selective reflection spectroscopy in the cholesteric solvent may be considered as a novel method of physico-chemical analysis, allowing us to obtain an insight into the nature of intermolecular interaction. Further studies are under way, involving non-mesogenic molecules forming intermolecular hydrogen bonds, charge transfer complexes, etc.

3. Conformational mechanism of helix inversion with temperature in non-steroidal cholesteric systems

Another example of the physico-chemical approach providing a description of unusual pitch–temperature behaviour in cholesteric systems is the temperature inversion of the helix sense in some derivatives of R,R-tartaric acid [25, 26] of the general formula

$$R-\!\!\bigcirc\!\!-CO.CHCHO.OC-\!\!\bigcirc\!\!-R$$
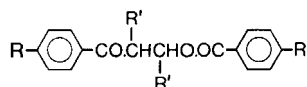
where R is 4-alkylcyclohexyl, 4-alkoxybenzoyl, 4-alkylbiphenyl, and $R' = CH_3$, $COOCH_3$, $COOC_2H_5$. This inversion cannot be explained by using the conventional compensation mechanisms [27, 28] or the other possibilities mentioned in [2, 12]. We assume, as in [25], that molecules of these compounds can exist in two different conformations A and B, which are in equilibrium

$$A \rightleftarrows B$$

in the cholesteric phase. If x_A is the mole fraction of A in the conformer mixture, the equilibrium constant K is

$$K = (1 - x_A)/x_A. \tag{7}$$

Then

$$\ln K = -\frac{\Delta H_k}{RT} + \frac{\Delta S_k}{R}, \tag{8}$$

where ΔH_k and ΔS_k are, respectively, the enthalpy and entropy of the conformational change. At temperature T

$$x_A = \frac{1}{1 + \exp(\Delta S/R)\exp(-\Delta H/RT)} \tag{9}$$

and the helical pitch p

$$p^{-1} = p_A^{-1}x_A + p_B^{-1}(1 - x_A), \tag{10}$$

where p_A^{-1} and p_B^{-1} are the intrinsic helical twisting powers of the conformers; they are determined by the geometry of how the chiral centres are situated with respect to the basic plane in each of the conformers, and can be calculated using the method of [5] cf. expression (23) of [1]). With the molecules in question, the relative positions of the carbonyl groups due to hindered rotation around C–O bonds are involved.

It follows from equations (9) and (10) that helix inversion ($p^{-1} = 0$) occurs at the inversion temperature

$$T_{inv} = \frac{\Delta H_k}{R(\ln|p_A/p_B| + \Delta S/R)}. \tag{11}$$

Estimating the values of the thermodynamic parameters in equation (11) ($\Delta H_k \approx 4\,\text{kJ}\,\text{mol}^{-1}$, $|\Delta S_k| \lesssim \Delta H_k/T$), we may obtain model dependences of T_{inv} (see figure 5). T_{inv} appears to be very sensitive to small changes in p_A/p_B and ΔS_k. Consequently, minor variations in molecular structure, which have no significant effect upon ΔH_k, can lead to strong shifts in T_{inv}, in accord with experiment [25, 26].
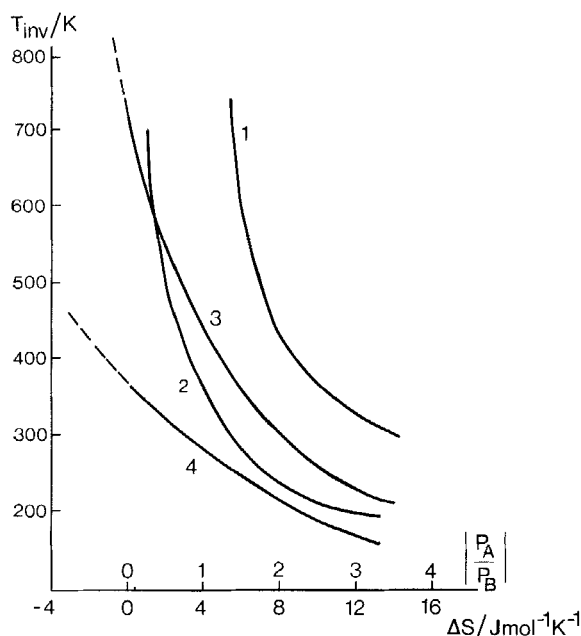

Figure 5. Helix inversion temperature as a function of the conformers' helical twisting power ratio (curves 1, 2) and the entropy of the conformational change (curves 3, 4) as obtained from model calculations. In these calculations $\Delta H_k = 4\,\text{kJ}\,\text{mol}^{-1}$ and (1) $\Delta S_k = 4\,\text{J}\,\text{mol}^{-1}\text{K}^{-1}$, (2) $\Delta S_k = 12\,\text{J}\,\text{mol}^{-1}\text{K}^{-1}$, (3) $|p_A/p_B| = 2$

The compounds considered have a helix inversion when they are used as individual chiral nematics and as optically active dopants (5–10 per cent) in a nematic [26]; T_{inv} values are rather close in both cases. This fact supports strongly the conformational mechanism, excluding any significant role of specific intermolecular interactions, which would be different for the two systems.

4.   Helical twist in induced cholesterics: some characteristic features due to chiral dopant–nematic matrix interaction

It is well known that the helical twist in an induced cholesteric systems (i.e. nematics doped with chiral substances) is very sensitive to the molecular structure of the dopant [29, 30]. For all types of optically active dopants we note, as the common feature, the presence of local distortions of the molecular orientation in the nematic. When the dopant concentration is small, chiral molecules interact via long range orientational order; the elastic deformation field is formed in the vicinity of the chiral molecule due to asymmetry induction [32, 33]. Thus, the helical twisting power $\beta = p^{-1}c^{-1}$ (p is the helical pitch and c is the dopant concentration) is determined not only by the asymmetry, but also by specific features of the dopant molecules incorporated into the nematic. If the dopant molecule is mesogenic or quasi-mesogenic (cholesterol esters, chiral nematics), a tendency towards parallel ordering may diminish the asymmetry effects. In contrast if the dopant molecule has no marked anisometry, orientational distortions may be quite significant. Generally, this may cause, apart from the induced T mode, an additional contribution to the nematic S mode (if $K_{22} \lesssim K_{11} < K_{33}$). The results of our experiments seem to agree with such an assumption.

We have studied the helical twisting power of chiral non-mesogenic derivatives of 4-X-benzylidene-l-menthone (XBM) with the general formula [34]

$$X-\bigcirc-\overset{\displaystyle H_3C-\ast\quad\ast-CH(CH_3)_2}{\underset{\displaystyle C\,H}{|}}\quad O$$
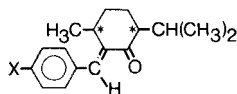
($X = OCH_3$ – MOBM; $X = NO_2$ – NBM; $X = C_6H_5$ – PhBM. 4-n-Alkoxybenzylidene-4'-n-butylanilines from C_1 to C_4 (MBBA, EBBA, PBBA and BBBA, respectively) were used as nematic solvents. The helical pitch for dopant concentrations up to 0·3 per cent was determined using the Cano wedge method and selective transmission in the I.R. region [35–37]. The helical twisting power β was determined for $T = T_{Chl} - 5°C$, where T_{Chl} is the cholesteric–isotropic transition temperature.

Figure 6 shows β as function of the alkyl chain length of the solvent molecule. An odd–even effect is clearly seen. The β values for different dopants increase in the order
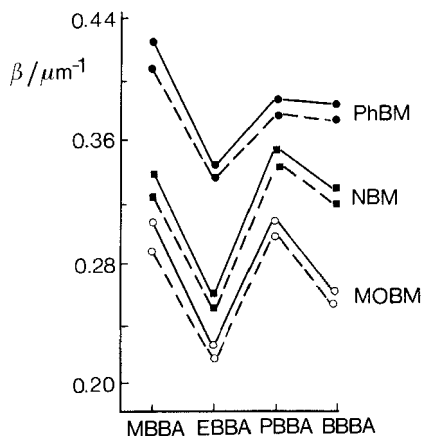

Figure 6.   Helical twisting power of benzylidene–menthone derivatives in a homologous series of nematic matrices at $T_{Chl} - T = 5°C$ (solid lines) and $T_{Chl} - T = 15°C$ (broken lines).
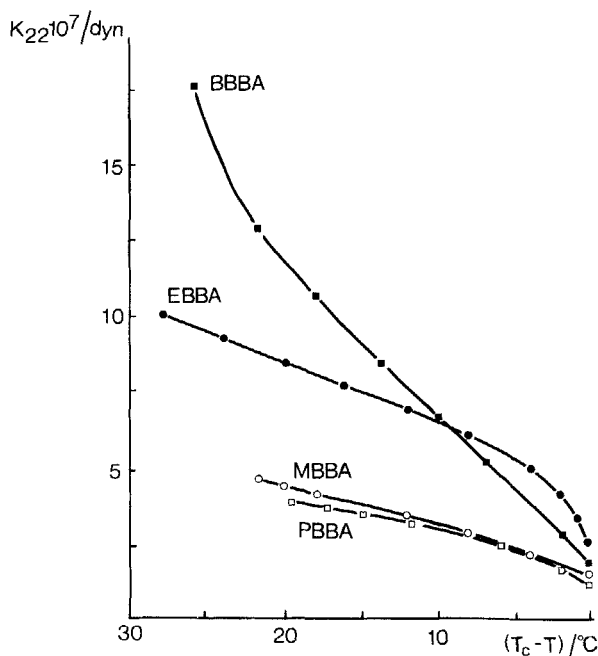
Figure 7. The temperature dependence of the twist elastic constant in the nematics studied.

MOBM < NBM < PhBM. EBBA appears to be the least twisted homologue. Based upon the generally accepted concept ($p^{-1} \approx K_2/K_{22}$), we have made a comparison with corresponding K_{22} values (see figure 7). The twist elastic constant, K_{22}, was determined using the cholesteric–nematic transition induced by the magnetic field of an N.M.R. ^{1}H spectrometer [38]; the anisotropy of the magnetic susceptibility $\Delta\chi$ was taken from [39]. K_2 values were determined from the slope of K_{22} versus p, with K_{22} and p values measured independently, as described previously (see the table). We note that K_2 values in the smectogenic BBBA are, unlike the p values, compensated allowing for pre-smectic phenomena, and reflect the intrinsic helical twisting power due to the molecular asymmetry. This point is discussed in detail in [37].

For non-smectogenic MBBA, EBBA and PBBA K_2 values do correlate with the K_{11}/K_{33} ratio (see figure 8). Bend and splay elastic constants of the nematics were determined using the Freedericksz transition in a magnetic field.

In further studies of helical twisting induced by different chiral dopants we have used MBBA as the nematic solvent and, in addition to the XBM compounds, cholesteryl propionate CP. Two types of experiments were carried out in a magnetic field. The temperature dependence of the induced pitch was measured using the Cano

Values of K_2 (dyn μm^{-1}) for the systems studied.

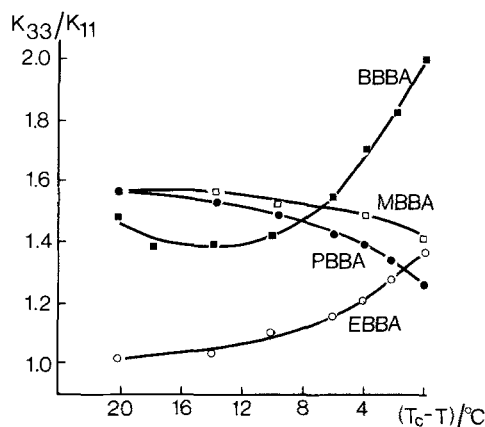| Dopant	Nematic			
	MBBA	EBBA	PBBA	BBBA
MOBM	2·1 ± 0·2	11·4 ± 0·4	3·0 ± 0·3	2·3 ± 0·2
NBM	2·6 ± 0·2	12·5 ± 0·4	3·5 ± 0·3	3·6 ± 0·2
PhBM	2·8 ± 0·2	13·5 ± 0·4	5·7 ± 0·3	3·8 ± 0·2

Figure 8. The bend to splay elastic constant ratio for the nematics studied

wedge (see figure 9), and the moduli of the elliptic integrals $E(k)$ and $K(k)$ from the Meyer–de Gennes equation [40, 41] were calculated:

$$\frac{p}{p_0}(T) = \left(\frac{2}{\pi}\right)^2 E(k)K(k), \tag{12}$$

where p_0 is the equilibrium pitch at $B_c = 0$. The $k(T)$ dependence thus obtained is shown in figure 10 as the broken lines. The validity of such an approach was checked by calculating $k(T)$ independently from
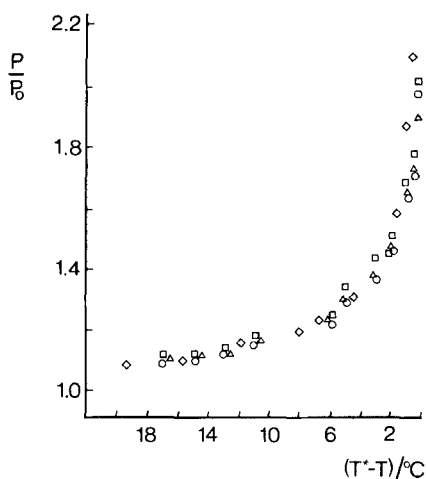
$$\frac{k}{E(k)} = \frac{B_c^0}{B_c} \tag{13}$$

Figure 9. Helical pitch as function of temperature in a constant magnetic flux density B_c for the induced cholesteric systems MBBA + XBM. $T^* = 40°C$; for all concentrations studied $p_0 = 10 \cdot 6 \, \mu m$. $B_c = 1 \cdot 3 \, T$ (O) $0 \cdot 21$ per cent MOBM; ($\triangle$) $0 \cdot 19$ per cent NBM, ($\square$) $0 \cdot 15$ per cent PhBM; $B_c = 0 \cdot 5 \, T$ ($\Diamond$) $0 \cdot 27$ per cent.
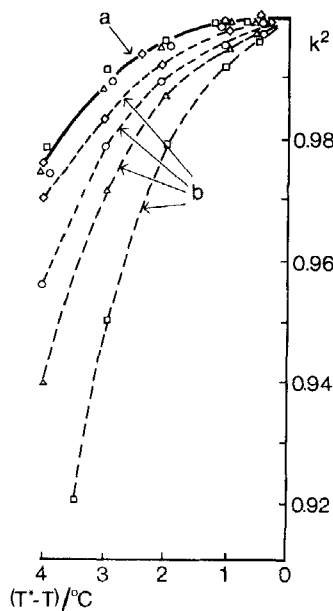
Figure 10. Temperature dependence of the intrinsic twist modulus measured using two independent methods: (a) Cano wedge (O, MBBA + 0·21 per cent MOBM; △, 0·19 per cent NBM; □, 0·15 per cent PhBM; +, 0·27 per cent CP); $B_c = 0·5\,T$. Solid line is calculated curve. (b) N.M.R. ^{1}H (O, MBBA + 0·3 per cent MOBM; △, 0·28 per cent NBM; □, 0·2 per cent PhBM; ◇, 0·7 per cent CP); $B_c = 1·5\,T$.

where B_c^0 is the critical magnetic field at $T^* = T_{ChI} - 5°C$,

$$B_c = \pi^2 (K_{22}/\Delta\chi)^{1/2} p_0^{-1}$$

was determined for $T < T^*$ from the values of K_{22}, p_0 and $\Delta\chi$, measured at these temperatures. The $k(T)$ curve thus obtained is shown in figure 10 as the solid line. The two plots practically coincide, suggesting that the temperature dependence of p/p_0 is universal for all of the dopants studied (see figure 9), with the range of the critical flux densities being $0·4 < B_c < 1·3\,T$.

In the second type of experiment, the k modulus was calculated from the ratio of second moments of the N.M.R. ^{1}H lines ($f = 60\,MHz$) in pure (N) and doped (N*) MBBA:

$$\frac{\langle \Delta f^2 \rangle_{N^*}}{\langle \Delta f^2 \rangle_N} = [P_2(\mathbf{n} \cdot \mathbf{B})^2]$$

$$= \frac{3}{2k^4}\left(1 - \frac{E(k)}{K(k)}\right) - \frac{3}{4k^2} + \frac{1}{4}. \tag{14}$$

Here [. . .] denotes spatial averaging from 0 to $p/2$. Equation (14) is valid if the distribution of the director along the induced helical axis is determined by a single azimuthal angle φ. Unlike the optical experiment, k values obtained from N.M.R. data are different for different dopants (see figure 10 (b)). For CP with its relatively low helical twisting power (about an order of magnitude less than that of PhBM [34]) $k(T)$ obtained from N.M.R. is the closest to the optical values.

The differences observed (see figures 10 (a) and (b)) suggest that the N.M.R. second moment is sensitive not only to deviations of the director from the magnetic

field by the azimuthal angle φ, but also to the quasi-nematic layers being inclined by an angle θ. It can be shown that, to a certain approximation,

$$[(\tfrac{3}{2}\cos^2\varphi\cos^2\theta - \tfrac{1}{2})^2] = (\tfrac{3}{2}[\cos^2\varphi][\cos^2\theta] - \tfrac{1}{2})^2. \qquad (15)$$

It is possible to evaluate the maximum θ values for different dopants from equations (14) and (15) using k values obtained from (p/p_0) (T). The results obtained may be summarized as

$\theta \approx 17°$ for PhBM ($c = 0.2$ per cent),

$\theta \approx 10°$ for MOBM ($c = 0.3$ per cent) and NBM ($c = 0.25$ per cent),

$\theta \lesssim 5°$ for CP ($c = 0.7$ per cent) within the accuracy limits.

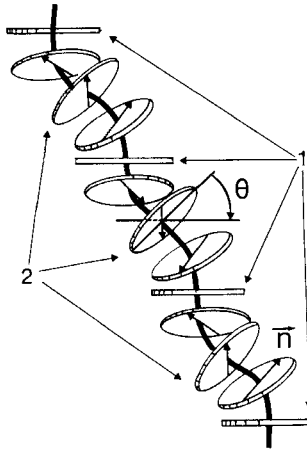The cholesteric structure for the case when θ_{max} is not negligible is shown in figure 11.

Figure 11. A tentative model for a cholesteric helix distorted by chiral dopants of a specific nature.

The mechanism of such helix distortions may be understood in terms of elastic deformations. If the dopant molecule is anisometric and compatible with the solvent, the elastic deformation field would be symmetric with respect to the director, inducing T modes and leading to the structure with $\theta \approx 0°$ (i.e. a conventional cholesteric). Van der Meer's chiral cog-wheel [5] is an extreme example of such a dopant molecule. In other cases, when the dopant molecules have a small anisotropy and significant molecular biaxiality, S modes are also induced. Benzylidene-*l*-menthone derivatives seem to be just such an example. We should note that light diffraction conditions in such systems are different for quasi-nematic layers with $\theta = 0°$ (sublattice 1) and $\theta = \theta_{max}$ (sublattice 2), leading to broader selective reflection bands with a possibility of multiple Bragg frequencies.

888   L. N. Lisetski and A. V. Tolmachev

References

[1] CHILAYA, G. S., and LISETSKI, L. N., 1986, *Molec. Crystals liq. Crystals*, **140**, 243.
[2] LIN-LIU, Y. R., SHIH, Y. M., WOO, C. W., and TAN, H. T., 1976, *Phys. Rev.* A, **14**, 445.
[3] LIN-LIU, Y. R., SHIH, Y. M., and WOO, C. W., 1977, *Phys. Rev.* A, **15**, 2550.
[4] VAN DER MEER, B. W., VERTOGEN, G., DEKKER, A. J., and YPMA, J. G. J., 1976, *J. chem. Phys.*, **65**, 3935.
[5] VAN DER MEER, B. W., 1979, Thesis, University of Groningen.
[6] KEATING, P. N., 1969, *Molec. Crystals liq. Crystals*, **8**, 315.
[7] BÖTTCHER, B., 1972, *Chem. Z.*, **96**, 214.
[8] GOOSSENS, W. J. A., 1970, *Phys. Lett.* A, **31**, 413.
[9] WULF, A., 1973, *J. chem. Phys.*, **59**, 1487.
[10] FINKELMANN, H., and STEGEMEYER, H., 1978, *Ber. Bunsenges. phys. Chem.*, **82**, 1302.
[11] LISETSKI, L. N., TOLMACHEV, A. V., and TISHCHENKO, V. G., 1978, *Pisma Zh. éksp. teor. Fiz.*, **23**, 205.
[12] CHILAYA, G. S., and LISETSKI, L. N., 1981, *Usp. fiz. Nauk*, **134**, 279.
[13] KUDRYASHOVA, T. P., LISETSKI, L. N., and CHISTYAKOV, I. G., 1979, *Kristallografia*, **24**, 998.
[14] CHILAYA, G. S., ELASHVILI, Z. M., LISETSKI, L. N., PILIASHVILI, T. S., and VINOKUR, K. D., 1981, *Molec. Crystals liq. Crystals*, **74**, 261.
[15] LISETSKI, L. N., 1982, *Ukr. Fiz. Zh.*, **27**, 1321.
[16] SCHAD, HP., and OSMAN, M. A., 1983, *J. chem. Phys.*, **73**, 5710.
[17] BELYAEV, V. V., ANTONYAN, T. P., LISETSKI, L. N., GREBENKIN, M. F., SLASHCHEVA, G. G., and PETROV, V. F., 1985, *Molec. Crystals liq. Crystals*, **129**, 221.
[18] ARAYA, K., and MATSUNAGA, Y., 1981, *Molec. Crystals liq. Crystals*, **67**, 809.
[19] ENGELEN, B., HEPPKE, G., HOPH, R., and SCHNEIDER, F., 1978, *Annl. Phys.*, **3**, 403.
[20] KUDRYASHOVA, T. P., LISETSKI, L. N., and CHISTYAKOV, I. G., 1978, *Zh. fiz. Khim.*, **52**, 2194.
[21] LISETSKI, L. N., and ANTONYAN, T. P., 1985, *Zh. fiz. Khim.*, **59**, 1813.
[22] KUDRYASHOVA, T. P., LISETSKI, L. N., and CHISTYAKOV, I. G., 1979, *Izv. Akad. Nauk SSSR, Ser. khim.*, p. 1731.
[23] PARK, J. W., BAK, C. S., and LABES, M. M., 1975, *J. Am. chem. Soc.*, **97**, 4398.
[24] PANIKARSKAYA, V. D., LISETSKI, L. N., and TISHCHENKO, V. G., 1980, *Zh. fiz. Khim.*, **54**, 1147.
[25] HEPPKE, G., LÖTZSCH, D., and OESTREICHER, F., 1987, *Z. Naturf. (a)*, **42**, 279.
[26] HEPPKE, G., GUNARATNE, M., LOETZSCH, D., OESTREICHER, F., and SCHEROWSKY, G., 1986, 11th International Liquid Crystal Conference, Berkeley, Poster θ-056-CH.
[27] BAESSLER, H., and LABES, M. M., 1970, *J. chem. Phys*, **52**, 631.
[28] GÖBL-WUNSCH, A., HEPPKE, G., and OESTREICHER, F., 1979, *J. Phys., Paris*, **40**, 773.
[29] GOTTARELLI, G., and SPADA, G. P., 1985, *Molec. Crystals liq. Crystals*, **123**, 377.
[30] CHILAYA, G. S., 1981, *Rev. Phys. appl.*, **16**, 193.
[31] BROCHARD, F., and DE GENNES, P. G., 1970, *J. Phys., Paris*, **31**, 691.
[32] SOLLADIE, G., and ZIMMERMANN, R. G., 1984, *Angew. Chem.*, **96**, 335.
[33] LOPATNIKOV, S. L., and NAMIOT, V. A., 1978, *Zh. éksp teor. Fiz.*, **75**, 261.
[34] KUTULYA, L. A., PIVNENKO, N. S., NEMCHYONOK, I. B., HANDRIMAILOVA, T. V., SEMENKOVA, G. P., BIBA, V. I., and TISHCHENKO, V. G., 1987, *Zh. obshch. Khim.*, **57**, 397.
[35] TOLMACHEV, A. V., and TISHCHENKO, V. G., 1982, *Zh. tekh. Fiz.*, **52**, 121.
[36] Tolmachev, A. V., and KUTULYA, L. A., 1987, *Zh. prikl. Spektrosk.*, **47**, 509.
[37] TOLMACHEV, A. V., LISETSKI, L. N., and TISHCHENKO, V. G., 1988, *Kristallografia*, **33**, 788.
[38] TOLMACHEV, A. V., GRINCHENKO, YU. A., and TISHCHENKO, V. G., 1988, *Kristallografia*, **33**, 786.
[39] DE JEU, W. H., CLAASSEN, W. A. P., and SPRUIJT, A. M. J., 1976, *Molec. Crystals liq. Crystals*, **37**, 269.
[40] DE GENNES, P. G., 1968, *Solid St. Commun.*, **6**, 163.
[41] MEYER, R. B., 1968, *Appl. Phys. Lett.*, **12**, 251.
[42] COLLINGS, P. J., GOSS, S. I., and McCOLL, J. R., 1975, *Phys. Rev.* A, **11**, 684.