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

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To cite this Article Fedoryako, A. , Popov, A. and Tolmachev, A.(1993) 'Induced helical structure of nematics in a magnetic field', Liquid Crystals, 14: 6, 1831 — 1836
To link to this Article: DOI: 10.1080/02678299308027718
URL: http://dx.doi.org/10.1080/02678299308027718

LIQUID CRYSTALS, 1993, VOL. 14, NO. 6, 1831–1836

Induced helical structure of nematics in a magnetic field

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Nematics MBBA, EBBA, PBBA, BBBA, 5CB, 8OCB and PCH5 doped with chiral 2-(4′-phenylbenzylidene)-*p*-menthan-3-one are studied. A numerical solution in terms of the Landau–de Gennes theory is obtained to describe the experimental temperature dependence of P/P_0, where P_0 corresponds to P in zero magnetic field. The angle of tilt θ from the plane perpendicular to the helical axis is evaluated and the domain wall energy in a constant magnetic field analysed. To take into account the helical structure deformation, the helicoidal order parameter G is defined, so that $G=0$ in the N phase and $G=1$ with $d\varphi/dz=$ const. and $\theta=0$ in the N* phase. The relaxation of the helical structure to the equilibrium state (N*→N) is shown to be determined by the domain wall energy with the magnetic field $H\neq 0$.

In nematics with chiral dopants, the spatial orientation of the director **n** has been shown to be characterized by an additional scale of spatial inhomogeneity with **n** being tilted from the plane perpendicular to the helical axis [1, 2]. The variation period l of this tilt angle θ is incommensurate with the helical pitch P (azimuthal twisting of **n**) with $l>P$. Thus, θ in a magnetic field defines the non-coplanarity of **n** in the domain wall, as distinct from the ordinary de Gennes 180° domain wall [3]. Obviously, the domain wall structure formed near the cholesteric–nematic transition (N*→N) retains both periodicity fragments. In order to test this assumption the structure of induced helical nematics described in previous research [4, 5] is studied using a magnetic field.

According to the Landau–de Gennes theory, the free energy density of the induced helical nematic N* is a power function of invariants of the tensor order parameter Q and its derivatives [6]

$$F=F_1+F_2(Q)+F_3(Q)+F_4(Q)\ldots, \tag{1}$$

where F_1 is independent of Q, but F_2, F_3 and F_4 contain Q in the second third and fourth powers, respectively.

The general description of the temperature-induced cholesteric–nematic transition in a constant magnetic field for N* with director $n=(\cos\theta\cos\varphi, \cos\theta\sin\varphi, \sin\theta)$ can be given by the expansion of the free energy F. Terms depending on Q have the following form:

$$\left.\begin{aligned} F_2&=S^2\left[\frac{1}{3}a+\left(\frac{d\theta}{dz}\right)^2\left(2L_1-\frac{2}{3}SL_3\right)+2L_1\cos^2\theta,\left(\frac{d\psi}{dz}-q_0\right)^2+\frac{1}{2}\Delta\chi H^2\cos^2\theta\sin^2\psi;\right.\\ F_3&=-\frac{2}{27}\beta S^3;\quad F_4=\frac{1}{9}\gamma S^4. \end{aligned}\right\} \tag{2}$$

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Making variations of F on the angle $\psi = \pi/2 - \phi$, we can obtain Euler–Lagrange's condition of equilibrium

$$d^2\psi/dz^2 = \tau_1^{-2} \sin(\psi)\cos(\psi), \tag{3}$$

where $\tau_1 = 2L_1S^2/(\Delta\chi H^2)^{1/2}$ is a novel magnetic correlation length, and $2L_1S^2 = [K_{22} + 1/3(K_{33} - K_{11})]$ is an effective elastic modulus. The final solution is obtained by the trivial method of using elliptical integrals of the first and second kind, $K(k)$ and $E(k)$, respectively

$$P/P_0 = (2/\pi)^2 K(k)E(k), \tag{4}$$

where k is in accordance with the demand of an energy minimum F in the magnetic field as

$$k/E(k) = HP_0/\pi^2(2L_1S^2/\Delta\chi)^{1/2}. \tag{5}$$

Equations (4) and (5) are the temperature analogy of the cholesteric–nematic transition under a field with the following conditions $P(T, H = \text{const.}) \to \infty$, $k \to 1$, $E(k) \to 1$, $K(k) \to \infty$ which are defined by a temperature dependence of the elastic moduli K_{ii} and an unperturbed helical pitch P_0.

Nematics MBBA, EBBA, PBBA, BBBA, 5CB, 8OCB and PCH5 were studied in the magnetic field range 0·05→1·3 T and the temperature range 20→80°C. The helical pitch was measured using the Cano wedge technique. Experimental P/P_0 versus H/H_c plots at constant temperature for all the nematics coincide and are in good agreement with the theoretical dependence following Meyer–de Gennes untwisting. The temperature dependences of P/P_0 ($H = \text{const.}$) are of different character. Results for some of the nematics which were studied here are shown in figure 1. Concentrations of the chiral

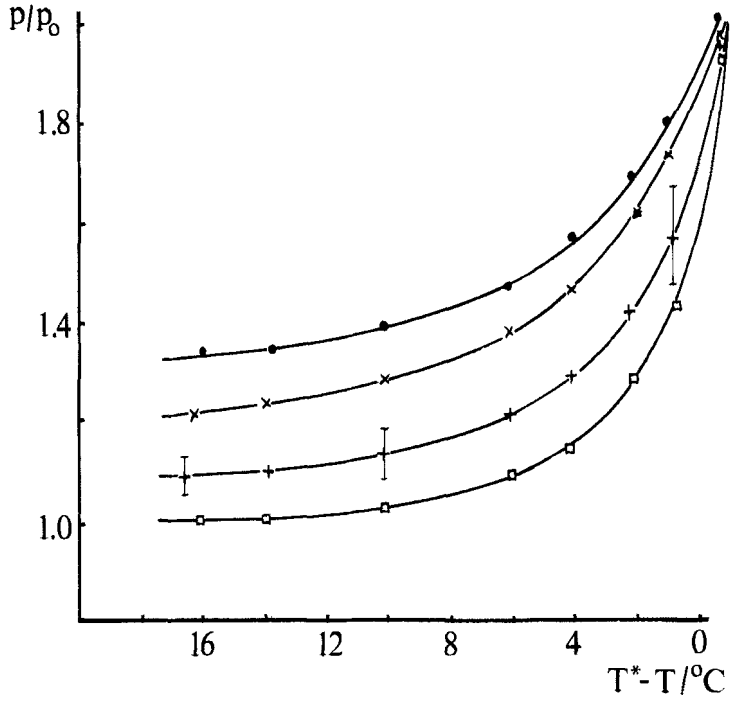

Figure 1. Untwisting of the helical structure of the N* phase with temperature in a magnetic field of 1·3 T and with pitch $P_0 = 11\,\mu$m: +, MBBA; ×, EBBA; ●, PBBA; □, BBBA.

dopant were varied so that the initial helical pitch $P_0 = 11$ μm for all the nematics. The helical structure of the N* phase for BBBA is perturbed by the magnetic field over the whole temperature range. For example, the N* phases of MBBA, EBBA and PBBA retain the structure perturbed at a lower temperature. The rate of relaxation to the equilibrium P_0 for the cybotactic nematic BBBA, where molecules are involved in strong short range interactions, is greater in comparison with the others.

Calculation of the dependences P/P_0 were performed using equations (4) and (5) and the experimental dependences $K_{ii}(T)$, $S(T)$ and $P_0(T)$ [4, 5]. The calculated P/P_0 shown as solid lines in figure 1 are in good agreement with the experimental data and reflect individual features of the structural changes in the N* phase under the external field. This also proves that the free energy expansion of F is correct.

The second moment of a NMR spectral line is characterized by high sensitivity to the relative orientation of the nuclear spin sub-systems and the magnetic field direction **H** [7]. This fact provides another method of studying spatial orientation of **n** in N* phases. It is possible to find the angle factor as a second moment ratio:

$$\langle \Delta\nu \rangle N^*/\langle \Delta\nu \rangle_N = \langle P_2(\mathbf{n}\cdot\mathbf{H})\rangle^2]. \tag{6}$$

The relaxation time (T_1) measured by the NMR technique exceeds by several orders the characteristic time of the director fluctuations; therefore the motional narrowing effect is negligible and only spatial averaging over the half pitch length $[\ldots] = (2/P\int_0^{P/2} \ldots dz$ is taken into account. For an explanation of the experimental results, it is proposed that at $T \leqslant T^*$, fragments of both incommensurate intervals P and l fall into a domain wall, so that the external orienting field affects P and l in the same way (i.e. $\varphi = \theta = 0$ out of the wall). It is convenient to express the angle factor in the spherical framework as $[(\frac{3}{2}\cos^2\varphi\cos^2\theta - 1/2)^2]$. Then the general expression for spatial averaging of the angle factor under non-zero φ and θ takes the form

$$[(P_2(\mathbf{n}\cdot\mathbf{H}))^2] = \frac{9}{2P}\int_0^{P/2} \cos^4\varphi\cos^4\theta\, dz - \frac{3}{P}\int_0^{P/2} \cos^2\varphi\cos^2\theta\, dz + \frac{1}{4}. \tag{7}$$

To carry out spatial averaging, it is necessary to know the dependence of $\varphi(z)$ and $\theta(z)$ on the external field. In the general case, this problem is complicated and has special theoretical interest. Therefore to explain the experimental results, we restrict ourselves to the following approximation. The temperature dependence of $\varphi(z)$ is assumed to be in accordance with the essentials of the Meyer–de Gennes model since equations (4) and (5) give a proper description of the experimental P/P_0 values in sufficiently thick samples. The magnetic field of the NMR spectrometer determines the tangential boundary conditions, which remain in some temperature range $\Delta T = T^* - T$. The temperature dependence of the modulus k was calculated from pitch measurements (for example, see [8]), and so $\varphi(z)$ was determined using equations (4) and (5) and taking into account: $d\psi/dz = (1 - k^2\sin^2\psi)^{1/2}/\tau_1 k$.

Further, the parameterization of $\theta(z)$ was assumed to be like that of $\theta = \theta_m \cos\psi$, where θ_m is the maximum value of the angle in the domain wall. Spatial averaging over the length $P/2 = 2k\tau_1 K(k)$ [9] gives

$$[(P_2(\mathbf{n}\cdot\mathbf{H}))^2] = \frac{1}{4K(k)}\left[\int_0^{\pi/2} \frac{9\sin^4\psi\cos^4\theta\, d\psi}{(1-k^2\sin^2\psi)^{1/2}} - \int_0^{\pi/2} \frac{6\sin^2\psi\cos^2\theta\, d\psi}{(1-k^2\sin^2\psi)^{1/2}} + K(k)\right]. \tag{8}$$

Only ψ directly depends on z, and θ_m is determined as a result of fitting of k values obtained from optical and NMR experiments. θ_m is assumed to be temperature

independent and evaluated at the temperature $T = T^* - 4°C$ by numerical solution of equation (8), substituting the modulus k from equation (4). For equal pitch values $P_0 = 11\ \mu m$ of the N* phase of MBBA doped with different optically active dopants, calculations give θ_m values not exceeding 13°. Inducing the N* phase in different nematics doped with 2-(4-phenylbenzylidene)-*p*-menthan-3-one, θ_m values were calculated (see later in the table). The accuracy of calculations does not exceed 2°.

In a previous study [4], it has been reported that the angle θ_m increases as a result of interaction between l and P when both intervals are approximating. In the present approach, it is shown that the structure of the N* phase in a magnetic field is determined by the periodicity of domain walls and also by its geometry. Therefore, for a proper description of the results obtained it is necessary to take into account both characteristics. It is convenient to use a helicoidal order parameter G[10] expressing the connection between the tensor properties of the induced helical structure and the unperturbed nematic:

$$G = 2(1 - [\langle \cos^2 \varphi \rangle])[\langle \cos^2 \theta \rangle]. \tag{9}$$

For perfectly ordered nematics, $G = 0$ (no deflection on **n** from boundary conditions) and $G < 1$ for different static deformations of **n** in the volume. The change in the magnitude of G means only a change of macroscopic symmetry of the nematic under external perturbation, and, in terms of this approach, does not include the orientational order parameter S.

Further, we shall find an expression for G in the approach used, i.e. we shall find solutions assuming φ and θ as independent variables. After the spatial averaging over the half pitch length, and adopting the same temporal averaging as in equation (7), the components of equation (8) are explicitly expressed as

$$[(\cos^2 \varphi)] = \frac{1}{k^2} - \frac{E(k)}{k^2 K(k)}, \tag{10 a}$$

$$[(\cos \theta^2)] = \frac{2}{P} \int_0^{P/2} \cos^2 \theta \, dz = \frac{1}{4K(k)} \int_0^{\pi/2} \frac{\cos^2 (\theta(\psi) d\psi)}{1 - k^2 \sin^2 \psi)^{1/2}}, \tag{10 b}$$

where $d\psi/dz = (1 - k^2 \sin^2 \psi)^{1/2}/\tau_1 k$ and $\theta = \theta_m \cos \psi$.

The calculated temperature dependence $G(T)$ on the previously obtained values θ_m (it is assumed that θ_m is constant over a narrow temperature range) is shown in figure 2 on a log–log scale. The meaning of G is elucidated from a comparison between the N* phases of EBBA and MBBA with the largest difference in twisting characteristics, i.e. the equilibrium value P_0 in the N* phase of EBBA is more distorted than in the N* phase of MBBA. However, in the latter case, values of G and dG/dT are smaller, i.e. relaxation of the N* phase to the equilibrium state ($G = 1$) proceeds more weakly. This is caused by the greater θ_m in the domain wall, and, subsequently, $[\langle \cos^2 \theta \rangle]$ is smaller.

Another important point can be found from the analysis of $G(T)$. The dependences $G(T)$ should be considered in two different sub-ranges: I (0→1·2°C) and II (1·2→4°C). It is observed for nematics (8OCB, PCH5, EBBA) with small θ_m that the dependence $G(T)$ changes more abruptly in region I. The slope of $G(T)$ corresponds to the variation in the effective magnitude of the elastic energy of the domain wall in the magnetic field, reflecting the competition between nematic deformation and untwisting of the N* phase. The region II corresponds to the quasi-stationary phase of the N→N* transition and is less interesting.

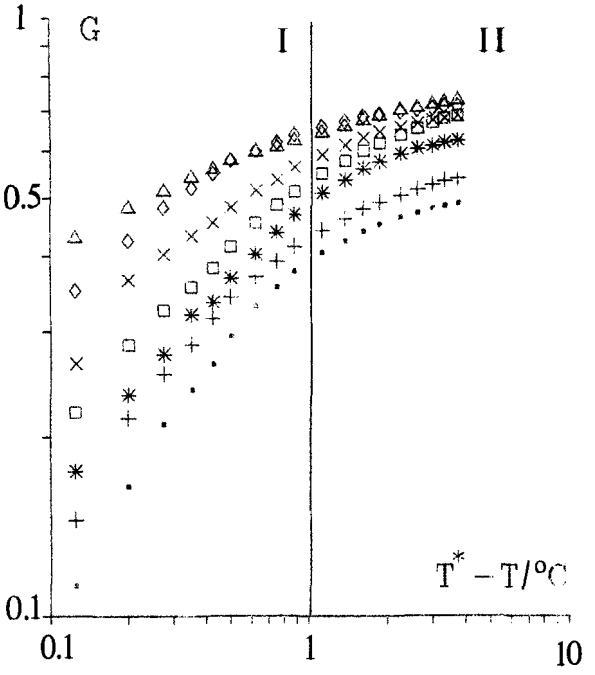

Figure 2. Temperature dependence of the helicoidal parameter G for various nematics: (▲, 8OCB; ◇, PCH5; ×, EBBA; □, BBBA, *, 5CB; +, MBBA; ●, PBBA).

The energy of a single domain wall is determined by subtracting from equation (2) the term q_0^2, giving no contribution to the energy deformation and integrating over the wall length ξ. Taking into account equation (3) we obtain

$$\frac{2F_2}{\Delta\chi H^2}=\tau_2^2\int_0^{\xi}\left(\frac{d\theta}{d\psi}\right)^2\left(\frac{d\psi}{dz}\right)^2 dz-2\tau_1^2 q_0\int_0^{\xi}\cos^2\theta\frac{d\psi}{dz}dz+\int_0^{\xi}\cos^2\theta\,dz$$

$$=2\tau_2^2\int_0^{\pi/2}\left(\frac{d\theta}{d\psi}\right)^2\left(\frac{d\psi}{dz}\right)d\psi-4\tau_1^2 q_0\int_0^{\pi/2}\cos^2\theta\,d\psi+2\int_0^{\pi/2}\frac{\cos^2\theta\,d\psi}{(d\psi/dz)}, \qquad (11)$$

where F_2 is the free energy per unit area of the wall and $\tau_2^2=(2L_1-2/3SL_3)S^2/\Delta\chi H^2$. The first and third terms represent the energy of deformation of nematics and the contribution due to interaction with the magnetic field, respectively. The second term describes deformation of the helical structure. Results for the approximate numerical evaluation of F_2 ($\simeq 10$ per cent) are given in the table.

Analysing the tabulated data, we can conclude that the relaxation of the helical structure to the equilibrium state (N*→N) has been shown to be defined by the domain wall energy at $H\neq 0$, the slope dG/dT being greater when θ_m in the wall is smaller.

N* phase	MBBA	EBBA	PBBA	BBBA	5CB	PCH5	8OCB
$\theta_m/^\circ$	13	$\leqslant 5$	12	12	10	8	$\leqslant 5$
$-F_2\times 10^3$/erg	11	14	11	12	12	15	16

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