

Effect of orientation order on the helical twist of cholesteric liquid crystals

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(Submitted 10 November 1977)

Pis'ma Zh. Eksp. Teor. Fiz. 27, No. 4, 205–207 (20 February 1978)

An anomalous temperature dependence of the pitch p of the helix has been observed for a number of substances that form cholesteric liquid crystals (CLC). A model is proposed that makes it possible to treat the $p(T)$ dependences in different cholesteric systems from a unified point of view.

PACS numbers: 61.30.Eb, 61.30.Cz

Up to now, no systematic experimental investigations have been made of the $p(T)$ dependences in CLC that undergo no phase transitions into the weak smectic- A phase. Practically all the available data pertain to CLC with narrow intervals of the existence of the mesophase and in which either the presence of components with opposite twist signs causes the cancellation phenomenon, or the character of the intermolecular interaction of the unlike components is not clear. An analysis of the $p(T)$ dependences is made complicated also by the fact that the proposed theoretical models predict both $dp/dT < 0$,^[1–3] and $dp/dT > 0$,^[4,5] and for each of these predictions it is possible to assume a different region of applicability in one concrete system or another.

In the present study we have determined, by the method of selective light reflection, the $p(T)$ dependences for a number of aromatic derivatives of cholesterine, which have broad intervals of existence of the mesophase and which form no smectics. Typical results are shown in Fig. 1.

It is easily seen that the obtained data cannot be interpreted on the basis of the known theories of CLC. Thus, the abrupt increase of $|dp/dT|$ near the isotropic-transition point T_u remains unclear. In the entire temperature interval, the values of $\alpha \equiv (1/p)(dp/dT)$ vary greatly from substance to substance, thus greatly contradicting Keating's theory which calls for $\alpha = -1/T$ for all CLC. In addition, the presence of a distinct correlation between the values of p and the values of the intrinsic pitches of other derivatives of cholesterine (see, e.g.,^[6]), obtained at various arbitrary temperatures, indicates that the absolute temperature T cannot serve as a natural parameter for the description of the thermodynamics of helical twisting in the cholesteric mesophase.

To explain these phenomena we can propose a model, in accordance with which the internal molecular field that hinders the rotational vibrations of the molecules becomes weaker with decreasing orientational-order parameter η determined in first-order approximation by the Mayer-Saupe theory. The equation of anharmonic rotational vibrations of a chiral CLC molecule will be written in the form

$$\ddot{\phi} + 3v\eta(T)l^{-1}\phi = ul^{-1}\phi^2, \quad (1)$$

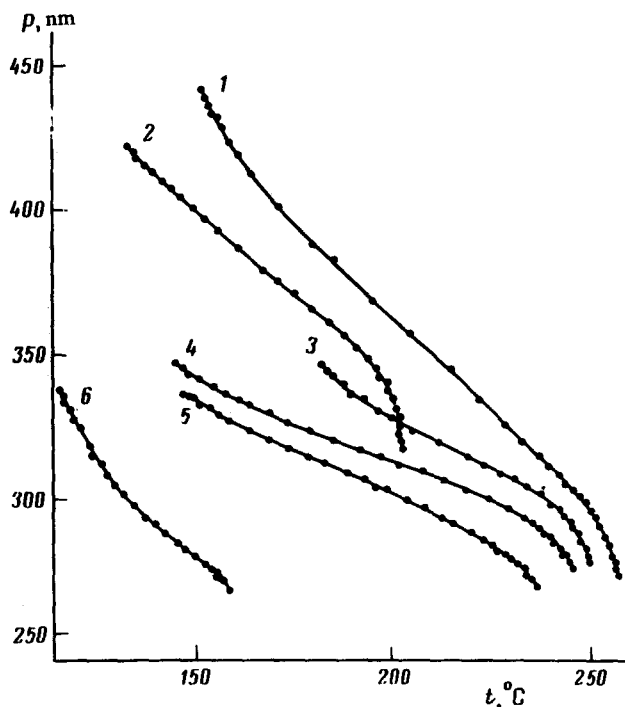


FIG. 1. Plot of $p(T)$: 1—*n*-nitrobenzoate, 2—cinnamate, 3—*n*-bromobenzoate, 4—*n*-chlorobenzoate, 5—*n*-methylbenzoate, 6—*m*-nitrobenzoate of cholesterine.

where ϕ is the angular coordinate of the rotational vibrations, v is the constant of the orienting interaction and is equal to $4.5415kT_u$,^[7] I is the moment of inertia of the molecule, and $u_v \equiv u/3v$ is the constant of the forces that cause the anharmonicity of the oscillations. After averaging over the time, the twist angle $\bar{\theta}_p$ ($\bar{\theta}_p = \theta_0 + \bar{\phi} = 2\pi d/p$, where d is the average distance between neighboring molecules in the direction of the optical axis and θ_0 is the twist angle corresponding to the minimum energy of the interaction of the chiral molecules) is defined as

$$\theta_p = \theta_0 + u_v \frac{t}{\eta(t)}, \quad (2)$$

where $t = 0.22019T/T_u$.

The linearity of the plots of the investigated relations in $\bar{\theta}_p$ vs. $t/\eta(t)$ coordinates (Fig. 2) is evidence in favor of the validity of Eq. (2). It can be assumed^[8] that the forces characterized by u_v and causing the anharmonicity of the rotational vibrations are due to steric repulsion of individual parts of the mesogenic molecules; this assumption agrees with the fact that the values of u_v increase with introduction of substituents that produce potential steric difficulties in the relative disposition of the molecules. We note that the ideas set forth here concerning the influence of the orientational order on the pitch of the cholesteric helix agree with the experimental values of η previously obtained by us^[9] for cholesteryl alkansates, which decrease regularly as the selective-reflection wavelength shifts towards the ultraviolet region with increasing hydrocarbon radical.

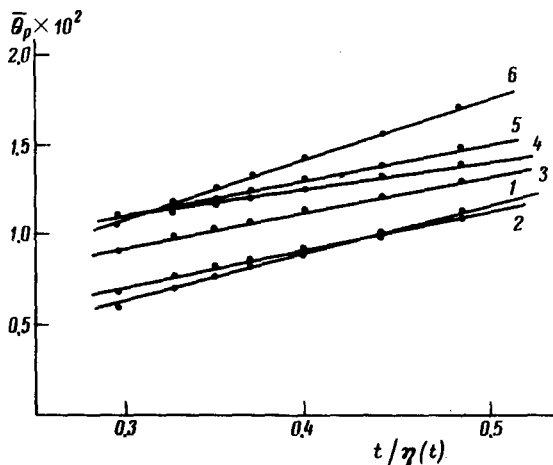


FIG. 2. Plot of θ_p against $t/\eta(t)$. The substances are analogous to those in Fig. 1. $u_v \times 10^2$: 1—1.36; 2—0.98; 3—1.08; 4—0.85; 5—1.0; 6—1.74. $\theta_0 \times 10^2$: 1—0.41, 2—0.55, 3—0.64, 4—0.78, 5—0.74, 6—0.52.

As to helically twisted mesophases with nematic compounds, we have $u_v < \theta_0$ as a result of the weak role of the steric factors, and the $p(T)$ dependence is determined by the mechanisms considered in^[4,5].

¹P. N. Keating, *Mol. Cryst. Liq. Cryst.* **8**, 315 (1969).

²B. Böttcher, *Chem. Ztg.* **96**, 214 (1972).

³B. W. van der Merr, G. Vertogen, A. J. Dekker, and J. G. J. Ypma, *J. Chem. Phys.* **65**, 3935 (1976).

⁴H. Stegemeyer and H. Finkelmann, *Naturwissenschaften* **62**, 436 (1975).

⁵L. N. Lisetskii, V. L. Timan, V. G. Tishchenko, and O. D. Kolotii, *Fiz. Tverd. Tela (Leningrad)* **19**, 3461 (1977) [*Sov. Phys. Solid State* **19**, 2023 (1977)].

⁶H. Baessler and M. M. Labes, *J. Chem. Phys.* **52**, 631 (1970).

⁷P. J. Wojtowicz, *RCA Rev.* **35**, 105 (1974).

⁸L. N. Lisetskii and V. G. Tishchenko, *Proc. Second Conf. of the Socialist Countries on Liquid Crystals, Solnechnyi bereg*, 1977, p. 172.

⁹A. V. Tolmachev, V. G. Tishchenko, and L. N. Lisetskii, *Fiz. Tverd. Tela (Leningrad)* **19**, 1886 (1977) [*Sov. Phys. Solid State* **19**, 1105 (1977)].