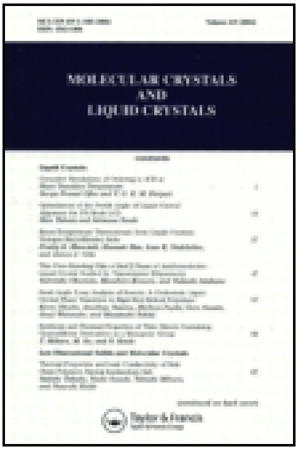

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Induced Cholesteric Systems: Pitch Depdendence on Temperature and Concentration

G. S. Chilaya [a] , Z. M. Elashvili [a] , L. N. Lisetski [a] , T. S. Piliashvili [a] & K. D. Vinokur [a]

[a] Institute of Cybernetics, Georgian SSR Academy of Sciences, S. Euti str. 5, Tbillsi, 280086, USSR

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Induced Cholesteric Systems: Pitch Dependence on Temperature and Concentration†

G. S. CHILAYA, Z. M. ELASHVILI, L. N. LISETSKI, T. S. PILIASHVILI and K. D. VINOKUR

Institute of Cybernetics, Georgian SSR Academy of Sciences, S. Euli str. 5, Tbilisi 380086, USSR

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Temperature dependences of the helical pitch have been studied for different induced cholesteric systems. It is shown that the sign of dP/dT in the same nematic solvent, may depend upon the nature of optically active dopants. For example, typical non-smectogenic nematics exhibit dP/dT values which are positive with l-menthol derivatives, and negative if the induced chirality is due to tygogenyn derivatives. A general theory of cholesteric pitch is developed providing an explanation of the experimental data in question as well as a description of pitch vs. concentration relationships in nematic—cholesteric mixtures. Also presented are some data for induced cholesteric systems with a smectogenic nematic component, where pretransitional phenomena with $P \to \infty$ are observed.

1 INTRODUCTION

Induced cholesteric mesophases, i.e. systems comprising nematic liquid crystals (NLC) and optically active dopants (OAD) are of growing importance for various applications. Still the nature of helical twisting in these systems remains rather obscure, reflecting both scarcity of experimental data and absence of a generally accepted theory of cholesteric mesophase.

Experimental data available (e.g. 1–6) are largely related to reciprocal pitch P^{-1} values obtained at a given concentration w of an OAD; and the values of helical twisting power (dP^{-1}/dw) for many OADs in a number of nematic solvents, have also been determined. Little attention, however, has been paid to pitch vs. temperature relationships. Small positive values of dP/dT observed

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for many NLC + OAD systems, were attributed to hindered rotation of chiral molecules around their long axes.[2] But the adequacy of this approach has not been established definitely with plenty of room left for alternative models,[7,8] resulting sometimes in even better fit to the experimental data.

And, speaking of steroidal molecules as OADs, with a lot of theoretical models proposed (see, e.g. 9–13), the nature of intermolecular forces causing, for example, cholesteryl chloride (CC), which forms right-handed helix by itself, to induce left-handed twisting in nematic solvents, has remained a mystery.

From the other point of view, a number of different theoretical approaches to description of helical twisting in cholesteric mesophases were suggested recently,[14–18] and induced cholesteric systems seem to be an excellent testing field for the models proposed.

And still another part of the problem, it is often desirable to obtain a cholesteric system with a strong pitch dependence on temperature (e.g. for use a temperature indicator). Mixtures of smectogenic cholesterol esters with large negative dP/dT values being used generally for the purpose,[19] it was of great interest to investigate possible NLC + OAD systems with the same behavior.

Here we present an outline of a general theory of cholesteric pitch which can readily be applied to interpret $P(T, w)$ curves in different helically twisted mesophases. Furthermore, experimental data on a number of induced cholesteric systems are presented and discussed.

2 THEORY

We start from the idea of (14, 15) to combine the approaches of Goossens and Keating in a general form of intermolecular potential. However, the authors of the idea tried to solve the problem in an over-generalized form, which made their expressions so complicated that they become virtually of no practical use. It was necessary to make some simplifications without losing the adequacy of the model.

Let us introduce a general expression for the angular dependence of intermolecular potential, bearing in mind two interacting molecules in adjacent quasi-nematic layers:

$$V(\theta) = -\eta\{\nu P_2[\cos(\theta - \theta_0)] + \sum_r u_r R_r(\theta)\} \tag{1}$$

where P_2 is the Legendre polynomial, η is the Maier-Saupe orientational order parameter; its value, as it was shown in (20, 21), are practically the same in both nematics and cholesterics, and the Maier-Saupe function is considered to be quite a good approximation to $\eta(T)$ dependences in cholesteric systems. The symmetry-breaking terms expressed by $R(\theta)$ functions are considered to arise from a slight inadequacy of the Goossens' theory-multipole expansions do not account for gemetric peculiarities of molecular structure usually referred to as "steric factors."

The averaged twist angle values are derived from the expression

$$\bar{\theta}_P = 2\pi a P^{-1} = \frac{\displaystyle\int_{-\pi/2}^{\pi/2} \theta \exp\left[-\frac{V(\theta)}{kT}\right] d\theta}{\displaystyle\int_{-\pi/2}^{\pi/2} \exp\left[-\frac{V(\theta)}{kT}\right] d\theta} \tag{2}$$

Now if we put $R(\theta) = \sin^3(\theta - \theta_0)$ and use the Maier-Saupe reduced temperature $t = kT/V = 0.22\,T/T_i$ (T_i is the isotropic transition point), model $p(T)$ curves are readily obtained with only two parameters involved: θ_0 and $u_v \equiv u/3v$. The first one expresses the Goossens' chirality, the second one—factors responsible for the rotational vibrations anharmonicity.

An analytical solution for the case $u_v \gtrsim \theta_0$ was obtained and proved to provide a quantitative description for cholesteric derivatives and their mixtures.[16,17] Another analytical solution was presented in (7) for the case $\theta_0 \gg u_v$ i.e. for negligible anharmonicities. That seems to be the case for NLC + OAD systems with $dP/dT > 0$.

Here we present the results of a numerical solution for different values of θ_0 and u_v (Figure 1). It is quite obvious that the sign of dP/dT depends upon factors causing asymmetry of $v(\theta)$ curve.

Introduction of the rotational order parameter $S_R(T) = \langle 1 - 2\sin^2\psi\rangle$ (2) brings in no qualitative changes. Relative values acquire a small positive addition, but the decisive role in determining its sign remains with the relative values of θ_0 and u_v. Absolute P values, however, may depend upon S_R greatly, as it has already been shown.[2]

Another kind of symmetry-breaking forces is represented by angle-dependent steric repulsions between the molecules of different species in nematic-cholesteric mixtures. If we approximate $R(\theta)$ by a step function in a narrow range of the angles of mutual orientation.

$$R(\theta) = \begin{cases} 1 & \theta_r - O < \theta < \theta_r + O \\ 0 & \text{for the other } \theta \text{ values} \end{cases} \tag{3}$$

We obtain correct magnitudes of extra twisting power values.[22] The source of these peculiar forces is presumably found in the so-called angular menthyl groups stretching out of the steroid ring plane and preventing an above-situated nematic molecule from taking orientations inside $\Delta\theta_r \equiv 2O$. With expression

$$\bar{\theta}_p(t) = \sum_i \sum_j \theta_{ij}(t) w_i w_j$$

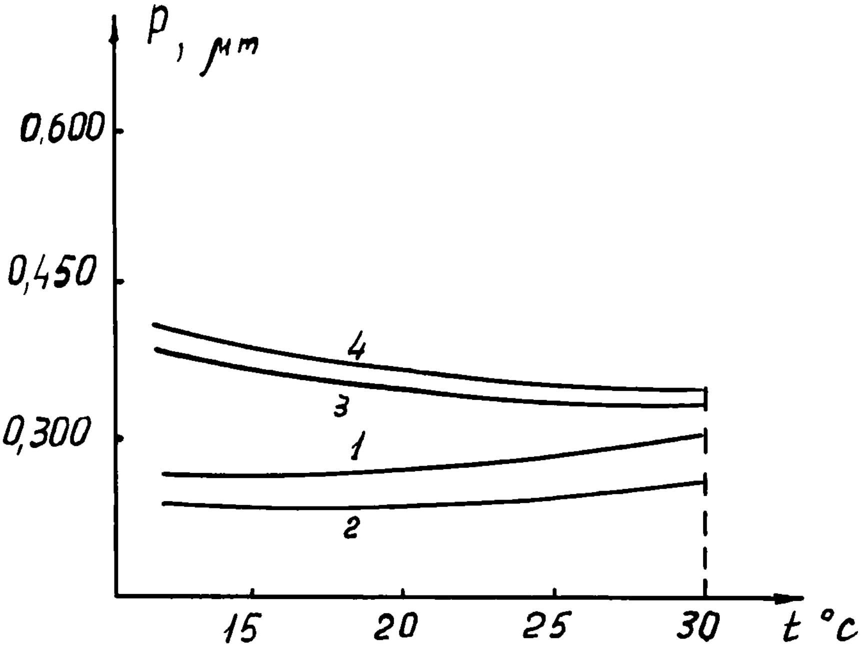


FIGURE 1 Model $P(T)$ curves for $a = 5$ Å and $T = 30°\text{C}$

1. $\theta_0 = 0.01$ $U_v = 0.005$
2. $\theta_0 = 0.01$ $U_v = 0.001$
3. $\theta_0 = 0.002$ $U_v = 0.02$
4. $\theta_0 = 0$ $U_v = 0.25$

we obtain model $P(T, w)$ curves as shown in Figure 2, where $\theta_r = 0.125$, $\Delta\theta_r = 0.15$.

This quite a non-trivial behavior has been observed experimentally in EBBA-CC systems.[23] As for nematic-cholesteric mixtures where the cholesteric component forms left-handed helix by itself (Figure 2, curve 5), the theory predicts a sign inversion of dP/dT i.e. one has to expect P increase with temperature when CC concentration w_{Ch} is low, while with higher w_{Ch} values dP/dT becomes negative.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Helical twisting power

Bragg scattering from the focal conic texture has been used to measure high P values, lower pitches being determined from selective reflection spectra. Details of the experimental procedure have been presented elsewhere.[24]

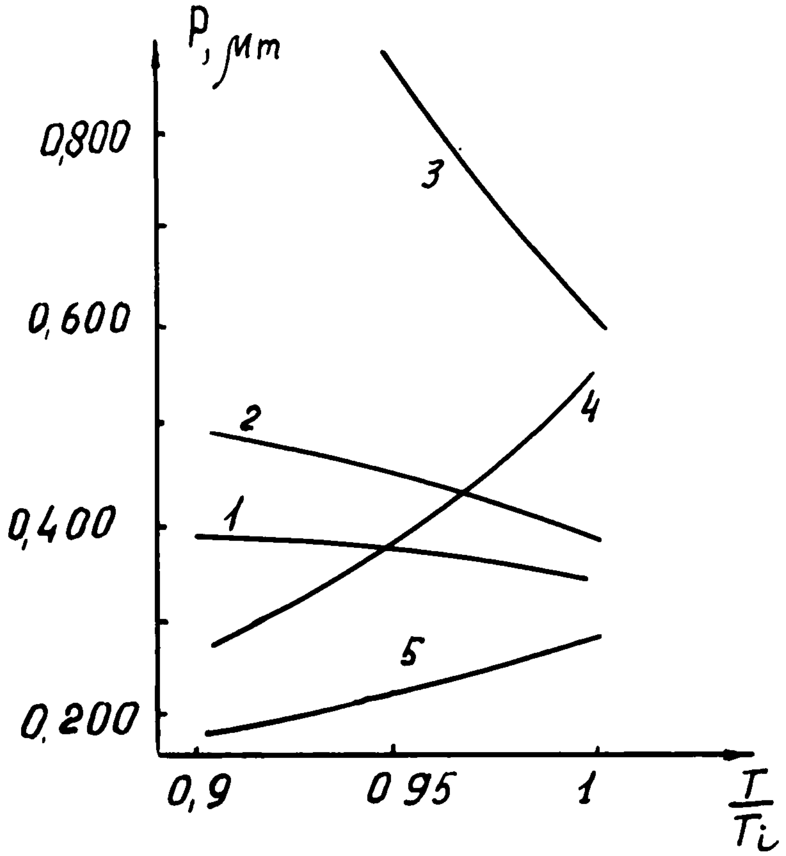


FIGURE 2 Model $P(T)$ dependences in nematic-cholesteric mixtures, for cholesterol derivatives forming a right-handed helix:

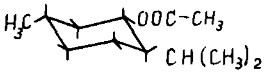
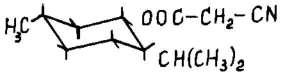
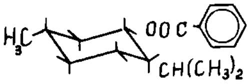
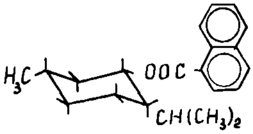
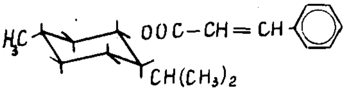
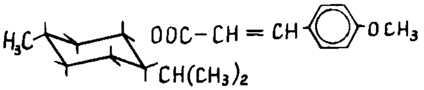
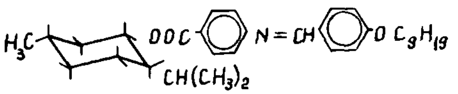
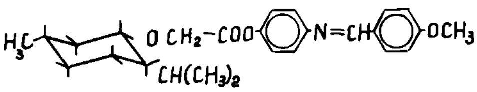
1. $W_{ch} = 1$ 2. $W_{ch} = 0.9$
3. $W_{ch} = 0.8$ 4. $W_{ch} = 0.3$
and a left-handed one:
5. $W_{ch} = 0.3$

The pitch is mainly determined by the value of molar rotation $M[\alpha]_D$ stereochemical and chemical nature of OAD.[2-5] Linear dependence of P^{-1} on w_m (molar concentration), i.e. $P^{-1} = Aw_m$ is observed at small concentrations. A characterizes the helical twisting power. The question arises, which of the above listed factors produces the greatest influence upon A.

We investigated the mixtures, in which the mixture of azoxycompounds with the mesophase range −4°C to 74°C served as NLC and l-methol esters were used as OAD (Table I).

TABLE I

The list of l-menthol derivatives.

	ОАД	Tпл.	$M[\alpha]_D$ $CHCl_3$	$A\ \frac{1}{\text{мм}\cdot\text{mol}\%}$
1		38-39	171	0,036
2		83-84	230	0,06
3		52-53	219	0,1
4		202-204 1mm	246	0,08
5		169-172 2mm	171	0,17
6		53-54	188	0,25
7		76-77	255	0,30
8		96-97	176	0,15

In Table I it is shown that OADs with molecules having a coplanar fragment, regardless of the $M[\alpha]_D$ value, have comparatively large value of A. Introduction of benzene ring into OAD molecule as well as an increase of conjugation length produces a great effect on the value of A. Helical twisting power of OAD N5 containing coplanar fragment is five times more than that of OAD

N1 at the equal value of $M[\alpha]_D$. Probably it is caused by plane compatability of NLC and OAD molecules. The value of A increases with the length of the conjugated chain (OAD N3, N5, N6, N7), and reduces when the conjugated long chain is cut, i.e. it is separated from the asymmetrical carbonic atom (OAD N8), $M[\alpha]_D$ reduces as well. While an increase of the coplanary fragment in width the value of $M[\alpha]_D$ also increases, but this produces little effect upon helical twisting power (OAD N4).

In the case of OAD molecule not containing coplanar fragment, the decisive influence is produced by the value of $M[\alpha]_D$. For instance, with the Cl atom being substituted in the molecule of OAD N1 by the CN-group (OAD N2) $M[\alpha]_D$ increases, causing correspondingly increase of A.

Therefore, the supposition is put forward that OAD which consists of molecules containing elongated conjugated coplanar fragments with large $M[\alpha]_D$ will have significantly larger value of A.

3.2 Influence of optically active dopant nature on pitch-temperature dependences

4-buthyl-4′-methoxyazoxybenzene (BMAOB) was used as a nematic solvent, while different l-menthol and tygogenyn derivatives as well as mesogenic cholesteryl formate served as OADs.

Figure 3 shows the results obtained with l-menthol derivatives as OADs. All the curves exhibit positive dP/dT values, which are in a qualitative agreement with the results of Stegemeyer and Finkelmann.[2] However, d^2P/dT^2 values differ very markedly for different OADs, which implies that the nature of $p(T)$ dependence may not be so straightforward. The results obtained with tygogenyn derivatives (Figure 4), exhibiting negative dP/dT values with the same nematic solvent, cannot be explained at all within the framework of earlier approaches.[2,6,7]

Using the theoretical model presented in Chapter 2, however, an explanation of the experimental results is readily given. The fact of $\bar{\theta}_p$ being dependent on reduced temperature t rather than on absolute temperature T implies that if the orientational order parameter values near T_i decrease more markedly than it is predicted by the Maier-Saupe theory, corresponding $|dP/dT|$ values would get an extra increase. Such $\eta(T)$ behavior is expected in systems with non-isomorphic components because of more diffuse character of phase transitions in this case. This, in turn, leads to extraordinarily high dP/dT values near T_i for the systems with l-menthyl oxalate and likewise derivatives.

One should note that for l-menthol derivatives $p - T$ curves have certain similarities with those of viscosity vs. concentration of corresponding dopants.[25] Unusually high dP/dT-values for induced cholesteric mesophases with l-menthyl oxalate close to T_i correspond to unusually high viscosity values for these systems with high OAD concentrations. An explanation of

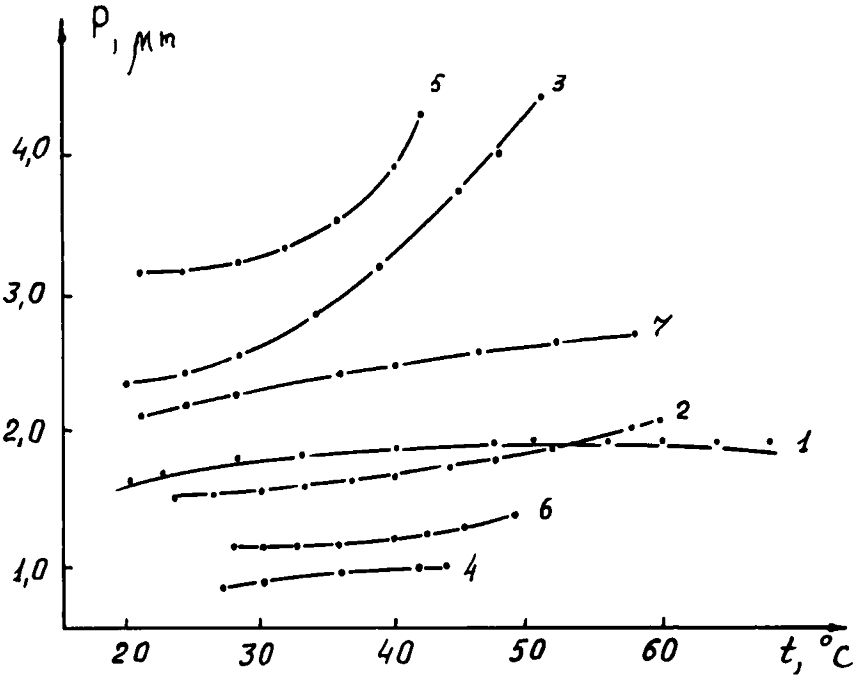


FIGURE 3 $P(T)$ dependences for induced cholesteric mesophases of BMAOB doped with 5% l-menthol derivatives: 1.4-methoxybenzylidene-4′-l-menthoxyacetanilide; 2. l-menthyl tosilate; 3. l-menthyl oxalate; 4. l-menthyl nitrobenzoate; 5. l-menthyl l-menthoxyacetate; 6. l-menthyl nitrobenzoate; 7. l-menthyl cinnamate.

this peculiarity may be presumably based on both pitch and viscosity being related to the orientational order parameter.

The $dP/dT < 0$ case (Figure 4) is considered as the result of tygogenyn and its derivatives introducing a strong source of rotational vibrations anharmonicity. With these substances the property in question is expected to be even more marked than with cholesterol derivatives (both higher u and lower ν leading to much higher u_ν). With cholesteryl formate (Figure 5) dP/dT becomes negative only with $w_{\mathrm{Ch}} = 0.25$, whereas with tygogenyn derivatives much smaller amounts of the chiral component cause P to decrease with temperature. The same dependence is observed in mixtures with l-DDCO.[26]

We may conclude that the nature of an OAD influences greatly not only the magnitude of dP/dT but even its sign. Thus, an adequate theory of $p(T)$ dependences in cholesterics should account for molecular structure peculiarities of a given system. In order to treat the question more qualitatively we have determined the values of θ_0 and u_ν for tygogenyn and its derivatives by means of fitting experimental data with the theoretical curves similar to those of Fig-

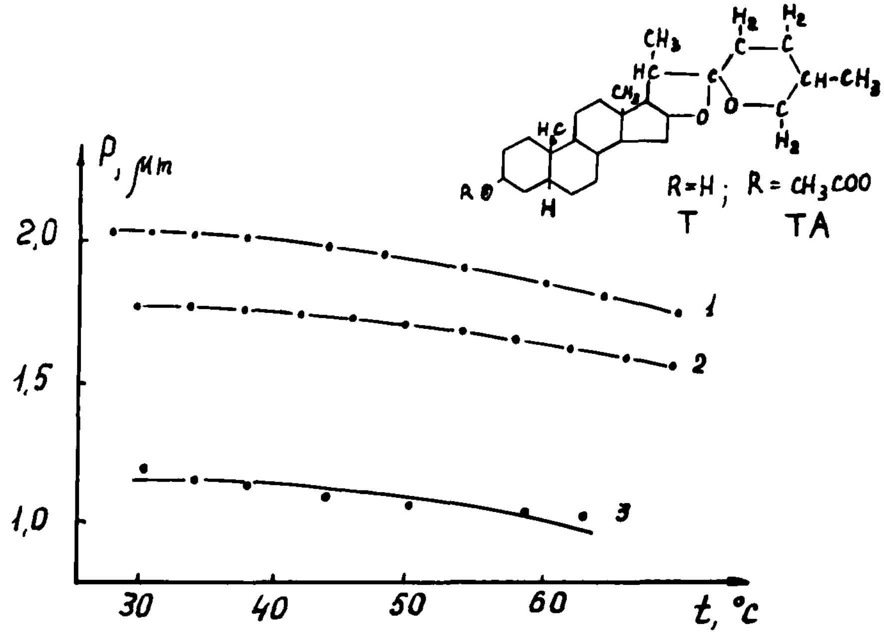


FIGURE 4 $P(T)$ dependences for induced cholesteric mesophases of BMAOB doped with tygogenyn and its derivatives: 1. tygogenyn acetate, 3%; 2. tygogenyn, 3%, 3. tygogenyn, 5%. Points represent experimental data, solid curves were fitted with the theoretical model, with $\theta_0 = 4.0 \cdot 10^{-2}$, $U_v = 5.3 \cdot 10^{-2}$ for tygogenyn and $\theta_0 = 4.2 \cdot 10^{-2}$, $U_v = 3.5 \cdot 10^{-2}$ for tygogenyn acetate.

ure 1 by the least-squares method (Figure 4). We see that u_v values for tygogenyn compounds are, in fact, considerably larger than those of cholesteryl esters (e.g. $u_v = 1.36 \cdot 10^{-2}$ for cholesteryl *p*-nitrobenzoate[16] or $u_v = 0.59 \cdot 10^{-2}$ for cholesteryl nonanoate.[17] As for θ_0 values, they reflect the sum of two remaining sources of helical twisting, apart from anharmonicity, i.e., Goossens' chirality and the extra twisting power due to nematic-cholesteric interactions; tygogenyn, being a steroid, also gives rise to the peculiar intermolecular forces expressed above by Eq. (3). More rigorous and explicit treatment of θ_0 and u_v values in different systems is to be considered elsewhere.

4 INDUCED CHOLESTERIC SYSTEMS WITH SMECTOGENIC NEMATICS

Now if we replace BMAOB with 4-nitrophenyl-4′-octyloxybenzoate (NPOOB), the *p*-*T* curves are changed dramatically (Figure 6). In both cases OADs are

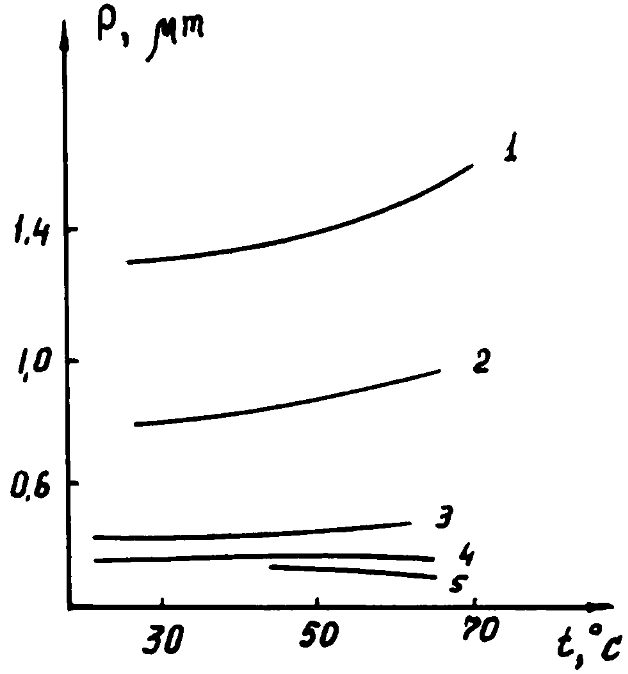


FIGURE 5 $P(T)$ dependences for induced cholesteric mesophases of BMAOB doped with cholesteryl formate:

1. $W_{ch} = 0.05$
2. $W_{ch} = 0.9$
3. $W_{ch} = 0.2$
4. $W_{ch} = 0.275$
5. $W_{ch} = 0.8$

the same, but the difference is that NPOOB is a smectogenic NLC, while BMAOB is not. A typical picture of pretransitional phenomena is observed in the systems with NPOOB, the cholesteric helix being untwisted near the phase transition point in a complete analogy with cholesterol esters, forming smectic-A mesophase. Other results of the same kind with 4-cyano-4′-octyloxybiphenyl (COOB) and 4-nonyloxybenzoic acid (NOBA) used as smectogenic nematics have been presented elsewhere.[27] One should note that the smectic mesophase formed by NOBA is of *C* and not of *A* type. This peculiarity, however, causes no significant changes in $p(T)$ curves.

All the systems mentioned above exhibited their "color play" only in infrared, being of no use for liquid crystalline thermoindicators. Recently we have managed, however, to obtain an example of the system exhibiting the same properties in the visible light range. Thoroughly purified BBBA has been used as a nematic solvent, while tygogenyn acetate has served as the most suitable OAD (Figure 7).

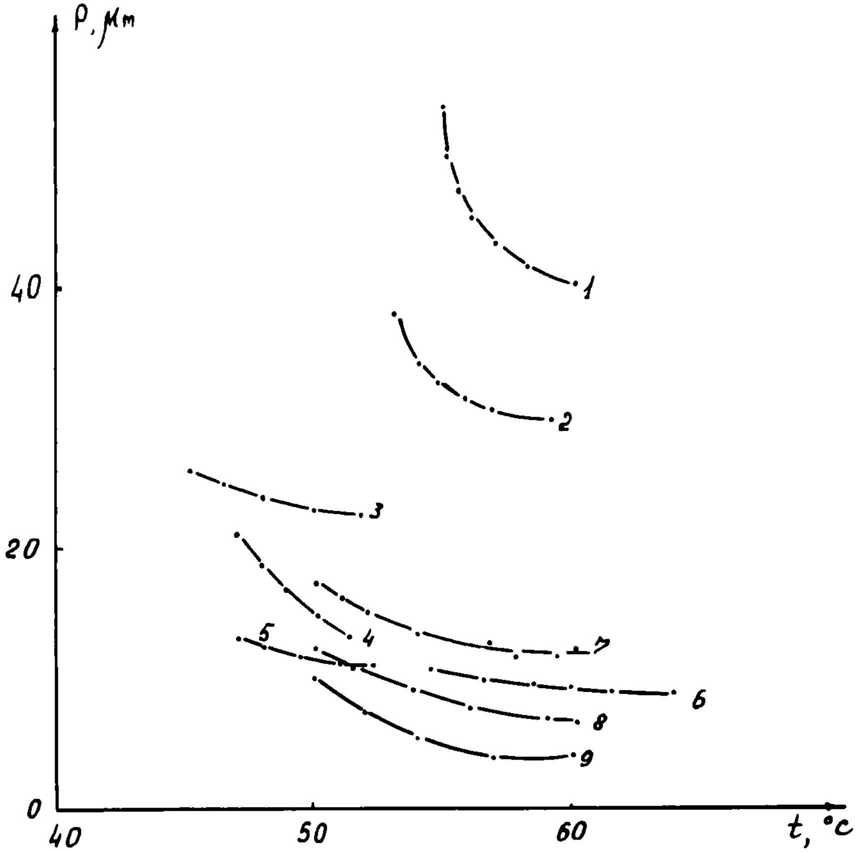


FIGURE 6 $P(T)$ dependences for induced cholesteric mesophases of NPOOB doped with l-menthol derivatives (1—5% 4-methoxybenzylidene-4′-l-menthoxyacetanilide, 2—5% l-menthyl benzoate, 3—5.3% l-menthyl tosilate, 4—6.6% l-menthyl benzoate, 5—5% l-menthyl nitrocinnamate). 6—5% tygogenyn acetate, and cholesteryl formate (7—5%, 8—7%, 9—10%).

5 CONCLUSION

It seems clear not that induced cholesteric mesophases can show the most varied types of thermochromic behavior, which enables them to complete successfully with the traditional mixtures of cholesterol derivatives. The study of such systems also enables us to present experimental proofs in favor of the theoretical model of helical twisting earlier introduced as "the modified Keating-Boettcher theory".[16,17] Further investigations are now under way, involving different nematic solvents and newly synthesized OADs with high helical twisting power values.

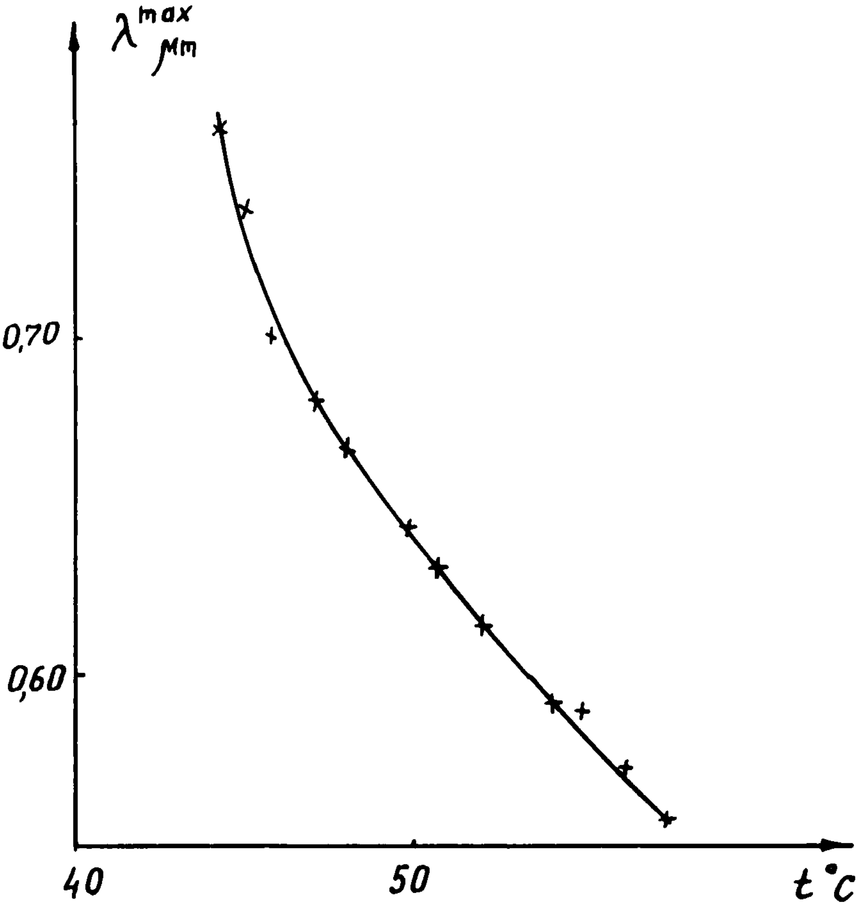


FIGURE 7 $\lambda_{max}(T)$ dependence for induced cholesteric mesophase of 4-*p*-buthoxybenzilidene-4'-*p* buthyl-aniline (BBBA) doped with 15% tygogenyn acetate.

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