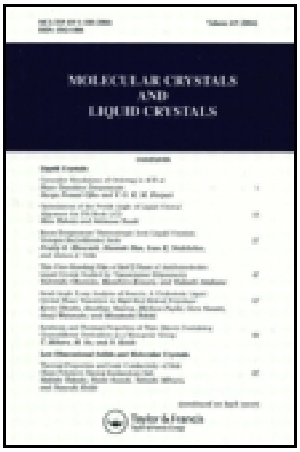

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Nematic-Chiral Mixtures for Application in Thermography

G. S. Chilaya [a] , Z. M. Elashvili [a] , S. P. Ivchenko [a] & K. D. Vinokur [a]

[a] Institute of Cybernetics of Academy of Sciences of Georgian SSR, S. Euli str., No. 5, Tbilisi, 380086, USSR

Version of record first published: 20 Apr 2011.

To cite this article: G. S. Chilaya , Z. M. Elashvili , S. P. Ivchenko & K. D. Vinokur (1984): New Nematic-Chiral Mixtures for Application in Thermography, Molecular Crystals and Liquid Crystals, 106:1-2, 67-71

To link to this article: http://dx.doi.org/10.1080/00268948408080179

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 67–71
0026-8941/84/1062-0067/$18.50/0

New Nematic–Chiral Mixtures for Application in Thermography†

G. S. CHILAYA, Z. M. ELASHVILI, S. P. IVCHENKO and K. D. VINOKUR
Institute of Cybernetics of Academy of Sciences of Georgian SSR, S. Euli str., No. 5, Tbilisi 380086, USSR

(*Received February 2, 1983; in final form July 28, 1983*)

A number of new chemically stable thermochromic mixtures of nematic liquid crystals with optically active mesogenic and non-mesogenic dopants are presented. It has been shown that colour-temperature characteristics of thermochromic mixtures depend on the nature of the nematic matrix (whether it is smectogenic, or not) and on the steroid structure of molecules of optically active dopants.

The changeability of the colour of mixtures of cholesterol derivatives with change of temperature is well-known. This property serves as the basis for work of various thermometer devices, applied in some branches of engineering as well as devices used for visualization of thermal distribution (for instance, in medical infrared diagnostics).[1–3] Unfortunately, cholesterol esters are not chemically stable, their-colour-temperature characteristics becoming worse with ageing. All this gives rise to the question about substitution of cholesterol derivatives by other chemical compounds. In search of new liquid crystalline materials it has been shown that nematogenic systems with inductive spiral structure, i.e. chiral nematics and nematic-chiral mixtures (NCM), are candidates for application in thermography. NCMs are preferable, since there is a rich choice of nematic liquid crystals (NLC) with wide temperature operating range and other physical properties and because a small quantity of optically active dopant (OAD) slightly changes the properties of initial NLC. Furthermore it is easier to prepare quite new NCMs than to synthesize new chiral nematics.

It is possible to use as OAD some liquid-crystalline materials, for instance, cholesterol derivatives, though it is only a partial solution of

---

†Paper presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 1982.

the problem. As cholesteryl esters are characterized by a small value of helical twisting power, for obtaining a NCM with selective reflection in visible range, it is necessary to introduce OAD in nematic matrix in large quantities—up to 25% by weight (see Table I; mixtures 1–3).

The application of some non-mesogenic optically active dopants seems to be more attractive. Since the introduction of a large amount of non-mesogenic OAD can destroy the liquid crystal phase, it is advisable to choose OAD characterized by a large value of helical twisting power and good solubility in the nematic matrix. To our knowledge there is no evidence in the present-day literature that non-mesogenic OAD in mixtures with NLC exhibit selective reflection of visible light. (As it was mentioned elsewhere,[4] the information[5] about *l*-menthol used as OAD in thermochromic mixtures was not correct. Furthermore, mixtures of NLC with *l*-DDCO become coloured only at an oblique incidence of light, i.e. at the oblique observation. Though non-mesogenic OADs[6] possess a high value of helical twisting power, the authors give no information about their application in thermochromic mixtures, apparently, because these OADs are not notable for good solubility.)

In the present work we used non-mesogenic *l*-menthol and tigogenin derivatives as OAD, because they are characterized by a high helical twisting power value and good solubility in nematics.[8,9] In our earlier reports[10–12] we investigated in detail the features of pitch-temperature

TABLE 1

No.	Composition of NCM	ΔT, °C	$\Delta\lambda_{\max}$, μm	Sign $d\lambda/dT$
1.	75% NLC 1 + 25% CF	23.0–78.0	0.550–0.614	+
2.	80% NLC 2 + 20% CD	12.7–79.7	0.670–0.740	+
3.	77% NLC 2 + 23% CA	23.5–73.5	0.618–0.664	+
4.	75% NLC 2 + 25% OAD 1	13.0–47.0	0.622–0.704	+
5.	92% NLC 2 + 8% OAD 3	17.5–39.0	0.596–0.652	+
6.	90% NLC 2 + 10% TA	17.7–68.5	0.720–0.590	–
7.	87.5% NLC 2 + 12.5% TA	17.5–68.5	0.612–0.526	–
8.	90.5% NLC 3 + 9.5% TB	18.3–70.5	0.690–0.546	–
9.	89.5% NLC 3 + 10.5% TA	26.0–67.9	0.720–0.658	–
10.	89.5% NLC 3 + 10.5% TV	31.3–68.0	0.698–0.605	–
11.	89% NLC 3 + 11% TD	45.7–64.0	0.728–0.638	–
12.	86% NLC 3 + 14% TD	20.1–58.8	0.605–0.490	–
13.	91% NLC 4 + 9% TV	36.6–65.3	0.732–0.614	–
14.	88% NLC 5 + 12% TV	50.0–73.1	0.720–0.640	–
15.	86% NLC 6 + 13.5% TV	47.0–62.5	0.692–0.520	–
16.	85% NLC 6 + 15% TA	43.1–61.4	0.750–0.555	–
17.	90.5% NLC 6 + 9.5% TB	58.8–66.6	0.740–0.642	–
18.	84% NLC 7 + 16% OAD 2	–16.3–0	0.480–0.420	–

dependences P(T) in NCMs, which contained exactly these OADs. It was shown that the value and the sign of dP/dT depend dramatically either on the nature of the nematic matrix, or on the geometric structure of the OAD molecules and intermolecular interaction in the system. Thus the necessity of consideration of the molecular structure of the whole system was shown.[13] Later it will be shown that our point of view on the given subject could be extended to NCMs with small value of pitch, which can be used as thermal indicator.

We used as NLC the following compounds: non-smectogenic-4-butyl-4′-octyloxy-NON-azoxybenzene (NLC 1), 4-butyl-4′-methoxy-NON-azoxybenzene (NLC 2), the mixture of one part of NLC 1 and two parts of NLC 2 (NLC 3); smectogenic-4-nitrophenyl 4-(octyloxy) benzoate (NLC 4), 4-carbonitrile-4′-octyloxybiphenyl (NLC 5), *N*-[(4-butoxyphenyl)methylene]-4-butylbenzeneamine (NLC 6) and also smectogenic mixture of 63% 4′-butyl-[1,1′-biphenyl]-4-carbonitrile with 37% 4-(hexyloxy)phenyl 4-butylbenzoate (NLC 7). The mesogenic smectogenic cholesteryl decanoate (CD), non-smectogenic cholesteryl formate (CF) and cholesteryl acetate (CA) as well as non-mesogenic *l*-menthol and tigogenin (spirostan-3β-ol) derivatives served as OADs. We used the following non-mesogenic OADs: *N*-[(4-methoxyphenyl)methylene]-4-menthoxyacetylbenzeneamine (OAD 1), *l*-menthyl 4-methoxycinnamate(OAD 2), *l*-menthyl-4-nitrocinnamate (OAD 3) and tigogenin acetate (TA), tigogenin benzoate (TB), tigogenin valerate (TV) and tigogenin decanoate (TD).

Table I lists the weight compositions of the thermochromic mixtures, their cholesteric temperature ranges, the intervals of wavelengths of the selective reflection and the signs of the $d\lambda/dT$ values. It should be emphasized that the cholesteric colours are spread over the entire cholesteric mesophase and these colours are reversible with temperature cycling.

Table I shows that the positive sign of $d\lambda/dT$, which was reported earlier for low concentrations of cholesterol derivatives,[14,15] also extends to the higher concentrations reported in this paper. Although the magnitude of $d\lambda/dT$ is smaller for the concentrations reported here, the pitch-temperature dependence in this case is determined by the average twist angle from neighbouring cholesteric planes. The average twist angle decreases with increasing temperature as a result of the associated reduction of the order along the long molecular axes.

At the same time in the mixtures, containing tigogenin derivatives as OAD, $d\lambda/dT < 0$. This is explained as the result of the steroid molecules of tigogenin and its derivatives being the source of rotational vibrational anharmonicity. The increase of anharmonicity of rotational vibrations of molecules with temperature leads to increase of relative twisting along the molecular axes in neighbouring quasi-nematic planes, which produces a corresponding decrease of the pitch of the cholesteric helix. It should be noted that tigogenin, in contrast to cholesterol, is a strong source of anharmonicity of rotational vibrations, the spiro-fragment ($C_8H_{14}O_2$), joined to the 16th and 17th atoms of carbon, bringing additional asymmetry into the molecule. Therefore, in mixtures with tigogenin derivatives untwisting of the cholesteric helix with decreasing temperature is observed.

We should emphasize that $d\lambda/dT$ decreases (by a factor of 3–5) with increasing concentration of *l*-menthol derivatives. On the contrary, $d\lambda/dT$ increases with increasing concentration of tigogenin derivative, that is in the framework of the suggested theory of intermolecular interaction in NCM. All the above-said concerns the non-smectogenic nematic matrix as well.

In a smectogenic nematic matrix a typical picture of pre-transitional phenomena is observed for all kinds of OAD; here $d\lambda/dT < 0$, which is caused by the unwinding of the cholesteric helix near the cholesteric-to-smectic transition point. In mixtures with tigogenin derivatives two mechanisms of unwinding exist, causing a considerable $d\lambda/dT$ value, which permits the mixtures of smectogenic NLC + tigogenin derivatives to compete successfully with cholesterol derivatives in various thermometer devices. Therefore, the obtained results prove our theoretical and experimental considerations about thermochromic behaviour of nematic–chiral systems and permit the continued search for new liquid crystalline materials as thermal indicators.

References

1. J. Fergason, *Sci. Am.*, **211**, 77 (1964).
2. L. N. Lisetski and V. G. Tischenko, In: "Cholesteric Liquid Crystals", Novosibirsk, p. 14 (1976) (Russ.).
3. A. S. Sonin, A. V. Tolmachev, V. G. Tischenko and V. G. Rak, *Zh. Eksp. Teor. Fiz.*, **68**, 1951 (1975).
4. C. Mioskowski, J. Bourguignon, S. Candau and G. Solladie, *Chem. Phys. Lett.*, **38**, 456 (1976).
5. H. Stegemeyer and H. Finkelmann, *Naturwissenschaften*, **62**, 436 (1975); H. Finkelmann and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **82**, 1302 (1978).
6. J. M. Ruxer, G. Solladie and S. Candau, *Mol. Cryst. Liq. Cryst.*, **41**, 109 (1978).
7. E. E. Topchiashvili and Z. M. Elashvili *et al.*, *Bull. Acad. Sci. Georgian SSR*, **83**, 101 (1976).
8. Z. M. Elashvili, T. S. Piliashvili and G. S. Chilaya, *Z. Chem.*, **19**, 453 (1979).
9. K. D. Vinokur, S. P. Ivchenko and G. S. Chilaya. *Zh. Tekh. Fiz.*, **49**, 1565 (1979); *Sov. Phys. Tech. Phys.*, **24**, 1870 (1979).

10. G. S. Chilaya, Z. M. Elashvili, T. S. Piliashvili, K. D. Vinokur and L. N. Lisetski, Advances in Liquid Crystals. Pergamon Press, Oxford, Budapest, p. 1185 (1980).
11. G. S. Chilaya, Z. M. Elashvili, S. P. Ivchenko, L. N. Lisetski and K. D. Vinokur. ibid, p. 1191.
12. G. S. Chilaya, Z. M. Elashvili, L. N. Lisetski, T. S. Piliashvili and K. D. Vinokur, *Mol. Cryst. Liq. Cryst.*, **74**, 261 (1981).
13. G. S. Chilaya, *Revue Phys. Appl.*, **16**, 193 (1981).
14. G. S. Chilaya, S. N. Aronishidze, K. D. Vinokur, M. D. Mkhatvrishvili and M. I. Brodzeli, *Kristallografiya*, **22**, 1280 (1977); *Sov. Phys. Crystallogr.*, **22**, 790 (1977).
15. L. N. Lisetski, G. S. Chilaya, K. D. Vinokur, V. G. Tischenko and V. D. Panikarskaya. *Ukr. fiz. Zhurn.*, **24**, 1082 (1979).