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Induction of Chirality by Doping Mesogens with Non-Mesogenic Chiral Dopant

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Use of chiral dopant in binary mixtures to induce ferroelectricity / chiral nematic phase is an easier way than the synthesis of ferroelectric or chiral nematic materials. Number of researchers have tried to induce chirality in the achiral mesogens by doping it with naturally occuring chiral compounds or their derivatives. Few binary systems were studied where one of the components is the non-mesogenic chiral dopant. In almost all the systems studied cholesteric phase (N^*) is induced with lowering in transition temperatures. The study provides means to induce chirality in mesogenic system by doping it with the derivative of naturally occurring chiral menthol.

Keywords: Non-mesogenic chiral dopant; Induced chiral mesophases

INTRODUCTION

Chiral liquid crystalline compounds have very interesting applications[1]. Much work is currently being done in this field. Synthesis of chiral liquid crystalline compounds involves high cost of starting materials which results into liquid crystalline materials of very high cost. Chiral liquid crystalline compound is also obtained by doping achiral mesogens with chiral mesogenic / non-mesogenic dopant. Neubert et al[2] have reported several liquid crystalline mixtures using binaphthyl derivative as a non-mesogenic chiral dopant. Kutulya et al[3] have presented the phase diagrams showing twist grain boundary states in some liquid crystalline systems based on the same non-chiral smectogenic matrix and different chiral dopants. In order to evaluate the chirality dependent properties pro-

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duced by chiral twin materials, systematic investigations on the physical properties of liquid crysralline mixtures of achiral host materials doped with small amount of various types of chiral twin materials have been carried out by Nishiyama and Yoshizawa[4]. Few reports appeared in literature on chiral liquid crystalline mixtures synthesized by using intermolecular hydrogen bonding[5,11] Drzewinski et al[12] have reported few two ring chiral benzoates with different terminal substituents being isotropic liquids or low temperature monotropic compounds as dopants inducing ferroelectricity in non-chiral SmC mixtures composed from esters.

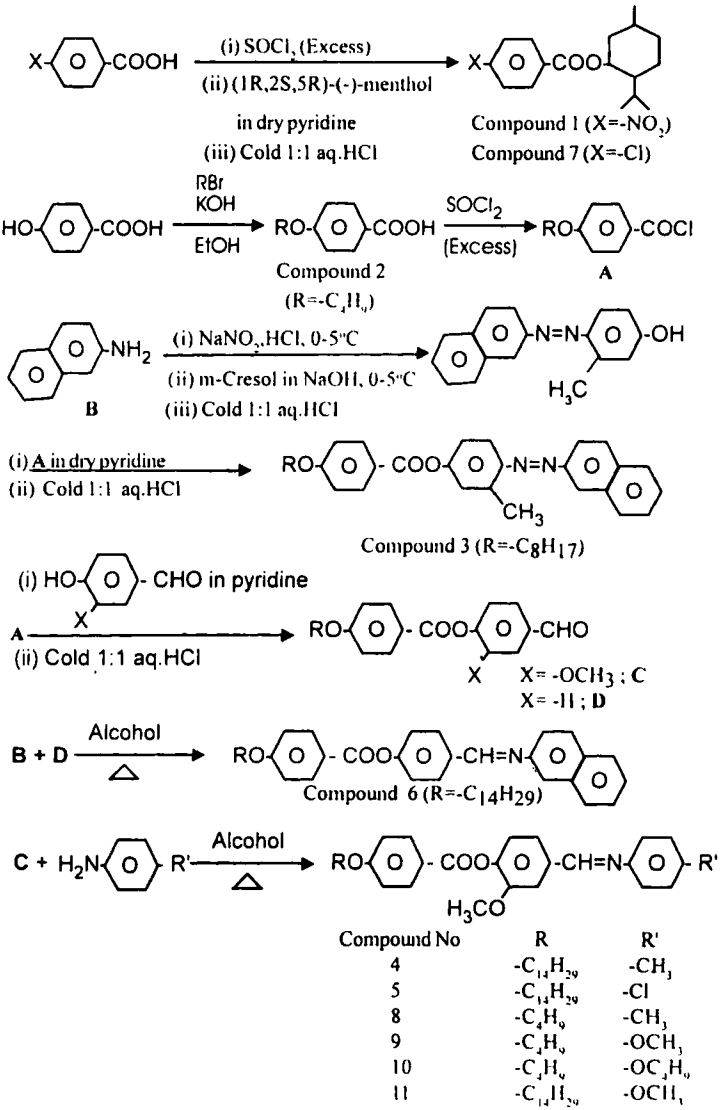
In this paper, we present the eleven new chiral liquid crystalline binary systems using non-mesogenic menthol based benzoate derivative as one of the component.

EXPERIMENTAL

Elemental analyses were performed on a Coleman carbon-hydrogen analyser and the values obtained are in close agreement with those calculated. IR spectra were determined via KBr pellets, using a Schimadzu IR-408 spectrophotometer NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer. Liquid crystalline properties were investigated on a Leitz Labourlux 12 POL microscope provided with a heating stage.

The eleven compounds listed below were prepared following the pathway shown in Scheme 1.

1. (1R, 2S, 5R)-(-) Menthyl 4-nitrobenzoate. (MNB)
2. 4-n-Butoxybenzoic acid. (4BA)
3. 4-(4′-n-Octyloxybenzoyloxy) 2- methyl phenylazo 2″-naphthalene. (8BMPAN)
4. 4-(4′-n-Tetradecyloxy benzoyloxy) 3- methoxybenzylidene 4″-toluidine. (14BMBT)
5. 4-(4′-n-Tetradecyloxy benzoyloxy)3-methoxybenzylidene 4″-chloroaniline. (14BMBCA)
6. 4-(4′-n-Tetradecyloxy benzoyloxy) benzylidene 2″-amino naphthalene. (14BBAN)
7. (1R, 2S, 5R)-(-) Menthyl 4-chlorobenzoate. (MCB)
8. 4-(4′-n-Butyloxybenzoyloxy) 3-methoxybenzylidene 4″-toluidene. (4BMBT)
9. 4-(4′-n-Butyloxybenzoyloxy) 3-methoxybenzylidene 4″-anisidene. (4BMBA)
10. 4-(4′-n-Butyloxybenzoyloxy) 3- methoxybenzylidene 4″-n-butyloxyaniline. (4BMBBA)
11. 4-(4′-n-Tetradecyloxy benzouloxy) 3-methoxybenylidene-4″ anisidene. (14BMBA)



Compound No	R	R'
4	$-C_{14}H_{29}$	$-CH_3$
5	$-C_{14}H_{29}$	-Cl
8	$-C_4H_9$	$-CH_3$
9	$-C_4H_9$	$-OCH_3$
10	$-C_4H_9$	$-OC_4H_9$
11	$-C_{14}H_{29}$	$-OCH_3$

SCHEME 1 Synthetic route to compound 1 to 11

General Procedure for the Synthesis of Chiral Dopant (Compound 1 and 7)

(1R, 2S, 5R)-(-) – Menthol (1.56g, 10 mmol) was dissolved in dry pyridine (10ml) and (1.85g, 10mmol) (for compound 1) / 4-chlorobenzoyl chloride (1.75g, 10 mmol) (for compound 7) in dry pyridine (10ml). The mixture was heated on water bath for an hour and was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid. The product was extracted with ether and ether layer was washed successively with water (2 × 30ml), 10% aqueous sodium hydrioxide (3 × 50ml) and water (3 × 30ml). It was then dried (Na_2SO_4) and evaporated on a rotary evaporator. The solid material obtained for compound-1 was crystallized repeatedly from methanol (3g, 88%), m.p. 65.0°C and the liquid material obtained for compound 7 was distilled under reduced pressure (2.8g, 84%), b.p. 182°C. The elemental data, IR and NMR spectral data of both the compunds are given below.

Elemental data

Compound 1: C 66.64, H 7.38, N 4.81%. $C_{17}H_{23}NO_4$ requires C 66.89, H 7.54 N 4.59%.

Compond 7: C 69.51, H 7.64%. $C_{17}H_{23}O_2Cl$ requires C 69.27, H 7.81%.

IR spectra: (V_{max}, Cm^{-1})

Compound 1: 1700, 1290 (-COO); 1540, 1320 ($-NO_2$); 1385, 1370 [$-CH(CH_3)_2$].

Compound 7: 1715, 1270 (-COO); 1385, 1370 [$-CH(CH_3)_2$]; 730 (C-Cl).

NMR spectra: (solvent $CDCl_3$, standard TMS, 60 MHz)

Compound 1: δ 0.9 (d, 9H, 3 x - CH_3), 1.2 – 1.8 (m, 9H, 6H of 3 x - CH_2 – and 3H of 3 x-CH-), 5.15(qunt., 1H, -COOCH-), 7.5 (d, 2H, ArH), 8.1 (d, 2H, ArH).

Compound 7: δ 0.9 (d, 9H, 3 x - CH_3), 1.25 – 1.8 (m, 9H, 6H of 3 x - CH_2 – and 3H of 3 x-CH-), 5.1(qunt., 1H, -COOCH-), 7.3 (d, 2H, ArH), 8.0 (d, 2H, ArH).

Compound 2 was prepared by the modified method of Dave and Vora[13]. Compound 3 was obtained by condensing n-octyloxybenzoyl chloride with 4-hydroxy 2- methyl phenylazo 2′-naphthalene (prepared by using conventional method of diazotization and coupling of 2-aminonaphthalene with m-cresol[14]) using pyridine as solvent[13]. Compounds (45,8,9,11)[15] and 10[16] are synthesized by the method reported in the literature and the transition temperatures of

all the compounds agree well with the reported value. The synthesis of compound 6 is described elsewhere[17].

Binary mixtures were prepared by the standard method[18].

RESULTS AND DISCUSSION

All the binary systems I-V contain MNB as component A. The transition temperatures are summarized in table I.

TABLE I Transition temperatures (°C) for system I – V

System	*Mole % of MNB*	*Transition temperatures (°C)*		
		SmA	*N* (Ch)*	*I*
I	3.24	–	147.0	155.0
	6.60	–	147.0	153.0
	10.09	–	146.0	153.0
	13.71	–	–	149.0
II	15.25	–	113.0	130.0
	28 80	–	(71.0)	118.0
	39.49	–	–	109.0
III	16.51	–	81.0	105.0
	30.79	–	82.0	92.0
	43 23	–	–	74.0
IV	17.38	(83.0)	98.0	118.0
	32.12	(84.0)[a]	94.0	105.0
	44.79	–	–	98.0
V	17.01	103.0	124.0	158.0
	31.57	102.0	122.0	149.0
	44.16	100.0	126.0	145.0
	55.17	93.0	123.0	130.0
	64.86	93.0	–	102.0

Values in parentheses indicate a monotropic transition.

a. SmA obtained on quenching.

Binary System I

Component B: 4 BA. Cr 147.0 N 160.0 I

The phase diagram is obtained by plotting mole percent composition of component A versus transition temperatures (Fig. 1a). The enantiotropic cholesteric mesophase (N^*) is induced even at very low mole percentage (3.24%) of the chi-

ral dopant MNB and is eliminated from the system when mole percent composition of component A reaches to 13.71 mole %.

Binary System II

Component B: 8BMPAN. Cr 114.0 N 148.0

The phase diagram (Fig. 1b) shows that induced enantiotropic cholesteric mesophase (N^*) becomes monotropic and is eliminated from the system when mole percent composition of component A reaches to 40 mole %.

Binary System III

Component B: 14 BMBT. Cr 81.0 N 120.0 I

The mixture exhibits induced enantiotropic cholesteric mesophase (N^*) upto 30 mole % of component A (Fig. 1c)

Binary System IV

Component B: 14 BMBCA. Cr (105.0) SmA 108.0 N 122.0 I.

The phase diagram (Fig. – 1d) shows that the induced enantiotropic cholesteric mesophase persists upto about 32.12 mole % of component A and the monotropic SmA mesophase survives only upto –20 mole % of component A. At 32 mole % of component A the SmA mesophase is obtained only on quenching.

Binary System V

Component B: 14 BBAN. Cr 101.0 SmC 162.0 N 194.0 I.

The binary phase diagram (Fig. 1e) shows that the enantiotropic cholesteric mesophase (N^*) is induced with lowering in transition temperatures upto 55 mole % of component A. It is very interesting to note that component B exhibits enantiotropic SmC mesophase whereas binary mixtures with chiral dopont (MNB) exhibits enantiotropic SmA in all the mixtures tried (i.e. upto 65 mole % of component A)

All the binary systems VI-XI contain MCB as component A. The transition temperatures are summarised in table II.

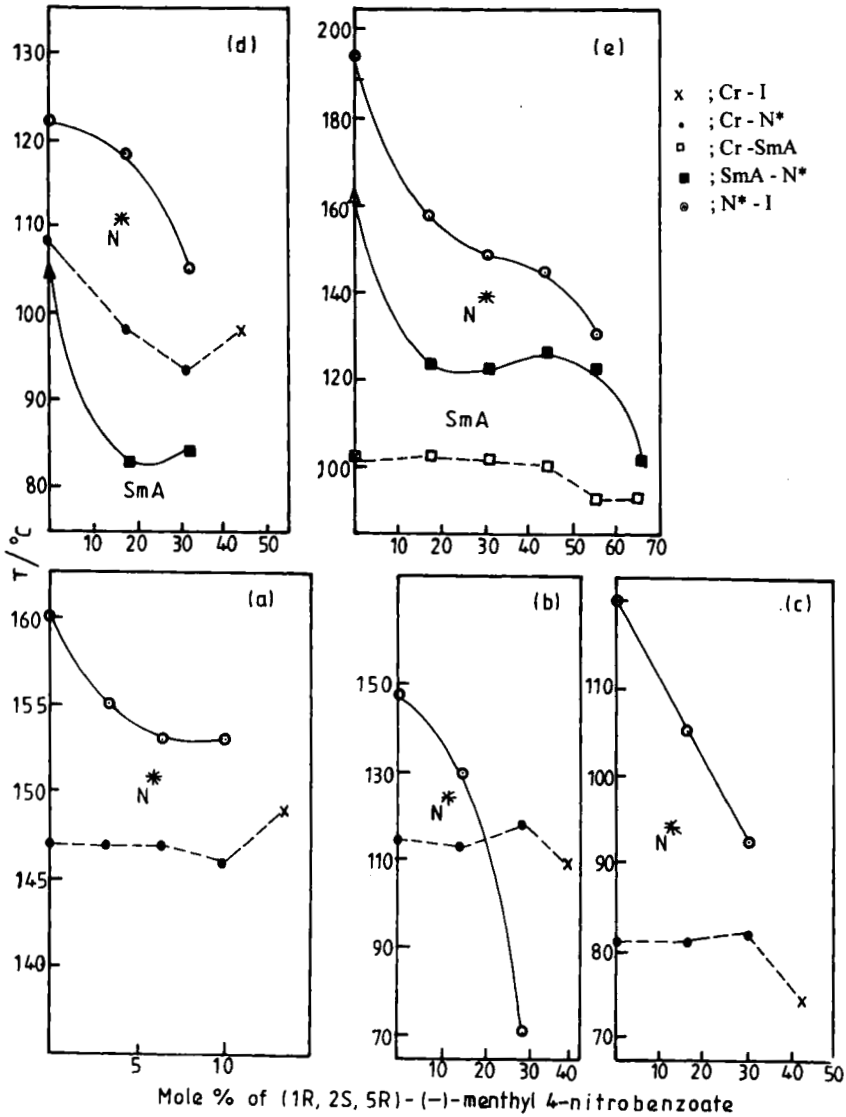


FIGURE 1 The phase behaviour of the system I-V

TABLE II Transition temperatures (°C) for system VI-XI

System	*Mole % of MCB*	*Transition temperature °C*	
		Ch(N)*	*I*
VI	2.47	146.0	155.0
	6.14	136.0	153.0
	12.14	133.0	149.0
	17.99	132.0	142.0
	23.70	129.0	131.0
	29.31	(118.0)	122.0
	34.77	(93.0)	120.0
VII	14.28	107.0	144.0
	26.03	110.0	138.0
	35.85	98.0	130.0
	44.18	97.0	124.0
	51.35	94.0	111.0
	57.57	(92.0)	104.0
VIII	12.33	116.0	151.0
	22.89	103.0	139.0
	32.05	98.0	121.0
	40.05	92.0	109.0
	47.11	(90.0)	98.0
	53.39	–	91.0
IX	12.74	129.0	180.0
	23.57	127.0	175.0
	32 87	122 0	167.0
	40.96	116.0	155.0
	48.05	108.0	146.0
	54.32	(96.0)	118.0
×	13.81	112.0	180.0
	25.28	110.0	177.0
	34.95	98.0	164.0
	43.22	97.0	157.0
	50.37	93.0	149.0
	56.61	(120.0)	132.0
XI	16.20	81.0	113.0
	28.98	78.0	106.0
	39.32	76.0	98.0
	47.86	75.0	88.0
	55.04	73.0	82.0
	61.15	(70.0)	79.0

Values in parentheses indicate a monotropic transition.

Binary System VI

Component B: 4BA. Cr 147.0 N 160.0 I

The enantiotropic cholesteric mesophase is induced even at very low percentage (2.47 mole %) of the chiral dopant and becomes monotropic at 29.31 mole % of chiral dopant (Fig. 2a).

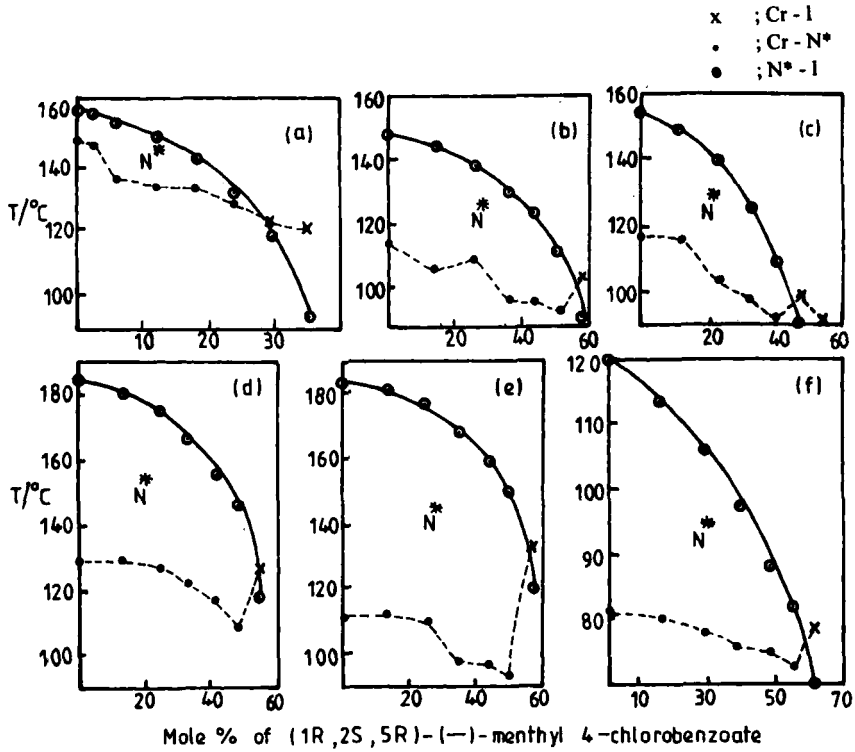


FIGURE 2 Phase behaviour of Binary system VI-XI

Binary System: VII

Component B: 8BMPAN. Cr 114.0 N 148.0 I

The mixture exhibits induced enantiotropic cholesteric mesophase upto 51.35 mole % of chiral dopant and then exhibit monotropic N^* mesophase at 57.57 mole % of chiral dopant (Fig. 2b).

Binary System: VIII

The mixture exhibits induced enantiotropic cholesteric mesophase upto 40.05 mole % of chiral dopant and then exhibit monotropic N^* mesophase which is eliminated from the system at about 53.39 mole % of chiral dopant (Fig. 2c).

Component B: 4BMBT. Cr 119.0 N 154.0 I.

Binary System IX

Component B: 4BMBA. Cr 130.0 N 184.0 I

The mixture exhibits induced enantiotropic cholesteric mesophase upto 48.05 mole % of chiral dopant and then exhibit monotropic N^* mesophase at 54.32 mole % of chiral dopant (Fig. 2d).

Binary System X

Component B: 4BMBBA. Cr 112.0N 183.0 I

The mixture exhibits induced enantiotropic cholesteric mesophase upto 50.37 mole % of chiral dopant and then exhibit monotropic N^* mesophase at 56.61 mole % of chiral dopant (Fig. 2e).

Binary System XI

Component B: 14BMBA. Cr 81.0 N 120.0 I

The mixture exhibits induced enantiotropic cholesteeric mesophase upto 55.04 mole % of chiral dopant and then exhibit monotropic N^* mesophase at 61.15 mole % of chiral dopant (Fig. 2f).

Common features of binary system I-XI

In all the systems I-XI enantiotropic cholesteric (N^*) mesophase is induced with lowering in transition temperature when the concentration of chiral dopant is small (<10–15 mole %). The induced cholesteric phase show the characteristic oily streak texture with brilliant colours. These colours were also seen in the visible region.

In case of binary system V the vivid colours were seen even at room temperature when melt was allowed to cool for crystallization. The binary system IV also exhibits monotropic SmA and systems V exhibits enantiotropic SmA mesophase (vivid focalconic texture) even though component B of system V exhibits enanti-

otropic SmC mesophase. Two phase regions (mesophase + isotropic phase) are observed in the case where the concentration of chiral dopant is high (>45 mole %). For simplicity the highest temperatures are considered for drawing binary diagrams.

CONCLUSION

In this paper we have described the preparation of two non-mesogenic menthyl ester as a chiral dopant and the induction of chiral mesophases in eleven systems by doping mesogenic compounds with this chiral dopant. However, due to branching in the chiralmenthylester, mesophase are adversely affected.

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