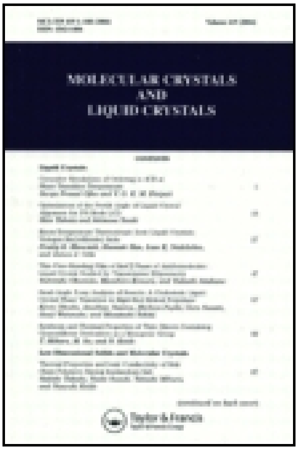

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Synthesis of Optically Active (+)-4-*n*-Alkylphenyl-4′-(4″-methylalkylbenzoyloxy)benzoates and Effect on Liquid Crystal Display Properties

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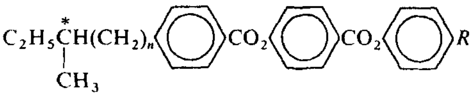
Three homologous series of optically active (+)-4-*n*-alkylphenyl-4′-(4″-methylalkylbenzoyloxy)benzoates (I) have been synthesized, *R* being normal alkyl group from C_1 to C_8 and $n = 1$, 2 and 3. Two additional compounds with R = CN and NO_2 and $n = 1$ were also synthesized. Their phase transition temperatures have been determined and the results showed that all of the compounds exhibited chiral nematic phase. The application of these compounds as dopants in ester mixture for the field effect display to reduce the response time and to eliminate the bounce effect is presented.



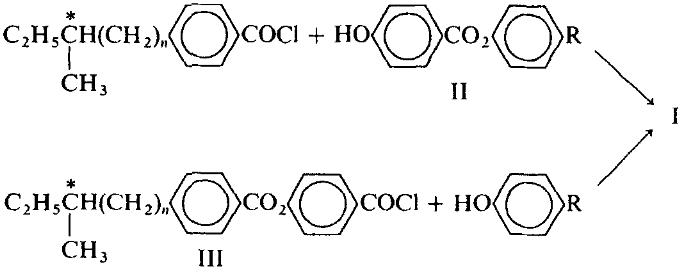
I

INTRODUCTION

The ester type liquid crystalline mixture with strong positive dielectric anisotropy and low threshold voltage was first reported in 1972.[1] The stability of ester mixtures with respect to moisture, oxygen and light was demonstrated to be greater than that of Schiff base mixtures.[2] With these advantages the ester mixtures have still not been widely used in manufacturing field effect liquid crystal displays. The main reason is that the ester mixtures show slow decay time upon removal of the electric field. This paper discloses the synthesis of a series of optically active ester compounds which can be used as dopants to reduce the decay time of ester mixtures in field effect display.

RESULTS AND DISCUSSION

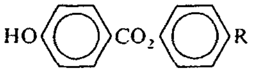
Two synthetic routes were used to prepare (+)-4-substituted phenyl-4'-(4"-methylalkylbenzoyloxy)benzoates (I).



The three series of alkyl derivatives were mainly synthesized by route 1 and the required intermediates (II) were prepared using the methods described by Gaylord[3] or Lowrance.[4] Table I presents the melting point for 4-alkylphenyl-4'-hydroxybenzoates (II) with the available data from the literature.[5] The cyano and nitro derivatives were only synthesized by route 2 because the corresponding intermediates in route 1 were not easily prepared

TABLE I

The melting points for 4-alkylphenyl-4'-hydroxybenzoates

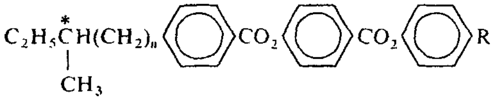


R	Melting point °C
CH_3	173–175
C_2H_5	157–159
C_3H_7	150–151 (148–150)
C_4H_9	143–144
C_5H_{11}	145–146 (145–147)
C_6H_{13}	134–136
C_7H_{15}	139–140
C_8H_{17}	126–127 (126–128)

Data in the parentheses are taken from Ref. 5.

TABLE II

Transition temperatures for (+)-4-substituted phenyl-4′(4-methylalkylbenzoyloxy)-benzoates



No.	*n*	*R*	Mesomorphic Range °C K–Ch	Ch–I
1	1	CH_3	90–91	164.8
2	1	C_2H_5	78–79	154.2
3	1	C_3H_7	80.8–81.2	162.4
4	1	C_4H_9	77.2–77.4	152
5	1	C_5H_{11}	67.5–68	152.7
6	1	C_6H_{13}	76.7–77.7	145
7	1	C_7H_{15}	76.4–77	140.8
8	1	C_8H_{17}	72.6–73.4	154.3
9	1	CN	103 –103.6	192
10	1	NO_2	131 –132	205
11	2	CH_3	109 –109.7	158.1
12	2	C_2H_5	103.8–104.5	147.5
13	2	C_3H_7	96.6–97.2	158
14	2	C_4H_9	85.0–85.7	145.9
15	2	C_5H_{11}	78.5–79.6	148.6
16	2	C_6H_{13}	73.0–74	145.5
17	2	C_7H_{15}	77.6–78.6	146.9
18	2	C_8H_{17}	80 –81	137.1
19	3	CH_3	90.7–91.7	148.5
20	3	C_2H_5	91.5–92.5	145
21	3	C_3H_7	73 –74.5	150.9
22	3	C_4H_9	78 –79.5	140
23	3	C_5H_{11}	68.7–69.5	140.5
24	3	C_6H_{13}	73.5–74.3	141.5
25	3	C_7H_{15}	77 –78	144.2
26	3	C_8H_{17}	74.7–75.7	137

K: solid, Ch: chiral nematic, I: Isotropic.

in the same manner. The phase transition temperatures for (+)-4-substituted phenyl-4′-(4″-methylalkylbenzoyloxy)-benzoates are summarized in Table II.

The results showed that all of the compounds exhibited chiral nematic phase with broad mesomorphic range. The phase transition diagram for the three series of alkyl derivatives is shown in Figure 1. The usual odd–even alternation of chiral nematic–isotropic transition was observed for the lower homologues ($R = C_1$–C_5). For the same alkyl group (*R*) the members of the 2-methylbutyl series ($n = 1$) show higher thermal stability with the exception of the C_6 and C_7 members. There was no regular trend for solid-chiral

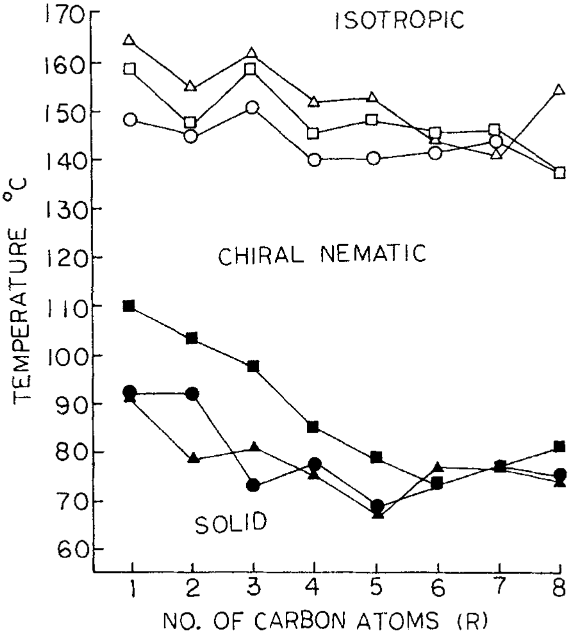


FIGURE 1 Phase transition diagram for (+)-4-*n*-alkylphenyl-4′-(4″-methylalkylbenzoyloxy)benzoates. ▲ (*n* = 1), ■ (*n* = 2) and ● (*n* = 3) solid–chiral nematic and △ (*n* = 1), □ (*n* = 2) and ○ (*n* = 3) chiral nematic–isotropic.

nematic transition with increasing alkyl chain length. Some lateral chloro substituted analogues of the 2-methylbutyl series ($n = 1$, $R = C_3, C_4, C_5, C_6$ and C_8) were reported by Klanderman and Criswell.[6] Their mesomorphic ranges were compared with the corresponding unsubstituted compounds of the present work. It was found that the solid-chiral nematic and the chiral nematic–isotropic transition temperatures for the former compounds are lowered about 0–45° and 50–70° respectively depending on the position of the chlorine atom.

A major problem of ester mixtures in field effect display application is that they have a relatively slow response time to return to the 90° twist after removal of the electric field. This decay time is particularly slow at higher voltages. Jakeman and Raynes[7] reported that the liquid crystal mixture of cholesteryl nonanoate, MBBA and cyano Schiff base showed decay time of the order of microseconds in the cholestric–nematic phase change effect. Addition of optically active ester compounds to ester mixtures to reduce response time has not been reported. The chiral nematic esters synthesized in this work have tight pitch and are suitable for using as dopants in ester mixtures to cause ester mixtures to become chiral nematic. By careful selection of the dopant concentration the pitch of ester mixture will be the desired four times cell spacing so that the imposed pitch of the ester mixture matches the cell spacing of the display. Because of this induced twist it is expected that the doped ester mixture will show improved response time.

A series of doped ester mixtures were prepared by adding dopants ($n = 1$, $R = C_1$–C_8, 0.8 wt. % and R = CN, 0.4 wt. %) to an ester liquid crystal composition of 75 weight percent cyanophenyl benzoates and 25 weight percent alkylphenyl benzoates. The ester mixtures were used to fill field effect watch displays with 11–12 μ cell spacing. The displays were cross polarized with reflectors at the bottom. Response time curves of percent absorbance versus time were measured by using an Olympus microscope fitted with a photometer and an oscilloscope with the light source at 35° from the normal. The measurements were made at 6 volts for $n = 1$, $R = C_1$–C_8 and 1.5 volts for R = CN at 32 Hz. Four response times (rise delay time, rise time, decay delay time and decay time) were determined from the response time curves. The results were shown in Table III. It is apparent that the decay delay and decay time of undoped ester mixture are slow compared to the doped ester mixtures.

A plot of percent absorbance versus time for ester mixture with and without dopant given in Figures 2a and 2b. The slow decay delay and decay time as well as undesirable bounce effect[8] upon removing the field is shown in Figure 2a. Fast decay time and no bounce were observed in the response time curve for same ester mixture with dopant ($n = 1$, $R = C_1$) as shown in

TABLE III

The response times for ester mixtures without and with dopant ($n = 1$, $R = C_1$–C_8[a] and CN[b]).

Dopants	Response times (ms)			
	T_{DR}	T_R	T_{DF}	T_F
0	30	215	185	265
C_1	25	205	60	220
C_2	40	190	130	195
C_3	30	220	115	185
C_4	25	230	100	225
C_5	35	225	130	190
C_6	30	190	110	210
C_7	25	210	40	250
C_8	20	230	40	240
CN	50	240	40	230

[a] Dopants concentration at 0.8 wt. % and response times measured at 6 volts.

[b] Dopant concentration at 0.4 wt. % and response times measured at 1.5 volts.

T_{DR} : rise delay time; T_R : rise time;

T_{DF} : decay delay time; T_F : decay time.

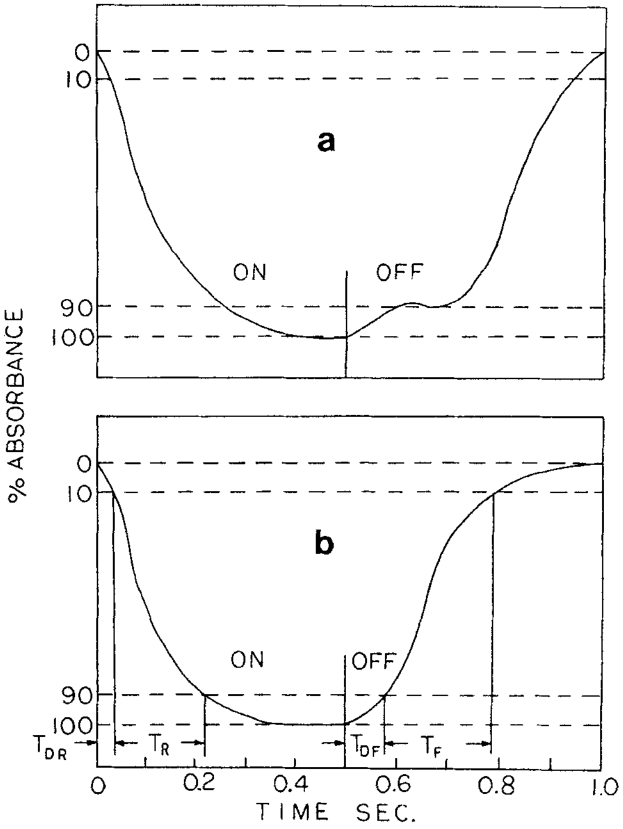


FIGURE 2 The response time curves for ester mixtures without (a) and with dopant (b) (n = 1, R = C_1, 0.8 wt. %).

Figure 2b. One disadvantage for dopant additions with weak positive dielectric anisotropy (R = C_1–C_8) is to increase the threshold voltage of ester mixture. Dopants with strong positive dielectric anisotropy (R = CN) is necessary to operate the display at low voltage.

CONCLUSION

The addition of chiral nematic ester to ester mixture reduces the response time of field effect displays comprising these mixtures. A dopant with strong positive anisotropy is required for low voltage operation. Bounce effect is eliminated by the natural twist in the display using the chiral dopant.

EXPERIMENTAL

The transition temperatures were measured by using an Olympus polarizing microscope equipped with a Mettler FP 5 temperature controller and FP 52 heating stage. The response time curves were determined by using an Olympus microscope fitted with a Model 301a photometer (Optical Associates Inc.) and a Model 1201A oscilloscope (Hewlett Packard).

Materials and syntheses

(+)-2-Methylbutylbenzene, (+)-3-methylpentylbenzene and (+)-4- methylhexylbenzene, (+)-4-(2′-methylbutyl)acetophenone, (+)-4-(3′-methylpentyl)-acetophenone and (+)-4-(4′-methylhexyl)acetophenone were prepared as previously described.[9,10,11]

(+)-4-(2′-*Methylbutyl)benzoic acid* Chlorine gas was passed into a stirred solution of sodium hydroxide (55 g, 1.37 m) in water (435 ml) kept below 0°C until the solution was neutral to litmus. A solution of sodium hydroxide (10 g) in water (15 ml) was added. (+)-4-(2′-Methylbutyl)-acetophenone (27.5 g, 0.145 m) was added in drops to the solution at 70–85°C with stirring. Stirring was continued for an additional hour. The excess sodium hypochlorite was destroyed by adding a solution of aqueous sodium bisulfite. After cooling to room temperature the reaction mixture was acidified with concentrated hydrochloric acid. The solid was collected and washed with water. The air dried crude product was crystallized from ethanol to yield (+)-4-(2′-methylbutyl)benzoic acid (19 g, 69 %), mp. 134–135°C.

(+)-4-(3′-*Methylpentyl)benzoic acid* (66 %), mp. 119.4–200°C.

(+)-4-(4′-*Methylhexyl)benzoic acid* (93 %), mp. 104.5–105°C.

(+)-4-(2′-*Methylbutyl)benzoyl chloride.* A mixture of (+)-4-(2′-methylbutyl)benzoic acid (19 g, 0.1 m) and thionyl chloride (30 ml) was refluxed for four hours. The excess thionyl chloride was distilled at ordinary pressure. The residue was distilled under vacuum to yield (+)-4-(2′-methylbutyl)-benzoyl chloride (19 g, 91.5 %), bp. 90–96°C/0.5–0.6 mm.

(+)-4-(3′-*Methylpentyl)benzoyl chloride* (76 %), bp. 105–109°C/0.3 mm.

(+)-4-(4′-*Methylhexyl)benzoyl chloride* (91 %), bp. 110–115°C/0.1 mm.

4-*n*-*Butylphenyl*-4′-*hydroxybenzoate*[3] Phosphoryl chloride (5.83 g, 0.038 m) was added to a mixture of 4-hydroxybenzoic acid (13.8 g, 0.1 m) and

4-*n*-butylphenol (15 g, 0.1 m). The reaction mixture was heated at 75–80°C with occasional swirling for four hours and then poured slowly with vigorous stirring into a solution of sodium carbonate (12 g, 0.113 m) in water (80 ml). The precipitate was collected and washed with water (4 × 20 ml). The etheral solution of the crude product was washed with sodium bicarbonate solution and water. The solvent was evaporated and the residue was recrystallized from carbon tetrachloride to yield 4-*n*-butylphenyl-4′-hydroxybenzoate (14.8 g, 55%) mp. 142–144°C.

(+)-4-*n-Butylphenyl-4′-[4″-(2‴-methylbutyl)benzoyloxy]benzoate* A solution of (+)-4-(2′-methylbutyl)benzoyl chloride (1.05 g, 0.005 m) in pyridine (4 ml) was added to a stirred solution of 4-*n*-butylphenyl-4′-hydroxybenzoate (1.35 g, 0.005 m) in pyridine (6 ml). After stirring for eight hours the reaction mixture was acidified with diluted hydrochloric acid and extracted with ether. The combined etheral solution was washed with water, diluted sodium hydroxide and water, then dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was recrystallized from ethanol to yield (+)-4-*n*-butylphenyl-4′-[4″-(2‴-methylbutyl)benzoyloxy]-benzoate (1.5 g, 67.5%) K–Ch 77.2–77.4°C, Ch–I 152°C.

(+)-4-[4′-(2″-*Methylbutyl)benzoyloxy]benzoic acid* A mixture of (+)-4-(2′-methylbutylbenzoyl chloride (8.4 g, 0.04 m) and 4-hydroxybenzoic acid (5.5 g, 0.04 m) in pyridine (60 ml) was stirred at −50°C for one hour. The reaction temperature was allowed to rise to room temperature and the reaction mixture was poured into a solution of concentrated hydrochloric acid (100 ml) and water (100 ml) at −10°C with stirring. Stirring was continued until the oily material was solidified. The solid was filtered and washed with 10% hydrochloric acid solution then with water. The air-dried crude product was crystallized from benzene to yield (+)-4-[4′-(2″-methylbutyl)benzoyloxy]benzoic acid (5.7 g, 46%), K–Ch 168–170°C, Ch–I 247°C.

(+)-4-[4′-(2″-*Methylbutyl)benzoyloxy]benzoyl chloride* A mixture of (+)-4-[4′-(2″methylbutyl)benzoyloxy]benzoic acid (5.7 g, 0.0182 m) and thionyl chloride (20 ml) was refluxed for four hours. The excess thionyl chloride was distilled and the residue was used in the following reaction without purification.

(+)-4-*Cyanophenyl-4′-[4″-(2‴-methylbutyl)benzoyloxy]benzoate* A solution of (+)-4-[4′-(2″-methylbutyl)benzoyloxy]benzoyl chloride (residue from above reaction) and 4-hydroxybenzonitrile (2.13 g, 0.018 m) in pyridine (20 ml) was stirred for eight hours. The reaction mixture was acidified with diluted hydrochloric acid and extracted with ether. The combined etheral solution was washed with water, diluted sodium hydroxide and water, then dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was recrystallized from ethanol to yield (+)-4-cyanophenyl-4′-[4″-(2‴-methylbutyl)benzoyloxy]benzoate (3.5 g, 47%) K–Ch 103–103.6°C, Ch–I 192°C.

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