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New liquid crystal compounds (+)-4-[5-(2-Methylbutyl)-1,3-dioxan-2-yl]phenyl 4-alkoxybenzoate

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New liquid crystal compounds, (+)-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl] phenyl 4-alkoxybenzoates (**5**), were synthesized. The mesomorphic behaviour of these compounds is compared with that of (+)-4-(5-alkyl-1,3-dioxan-2-yl)-phenyl 4-(2-methylbutoxy)benzoates (**6**). While compounds **6** exhibited a chiral smectic C phase, the corresponding compounds **5** did not. This might mean that for the appearance of a chiral smectic C phase in these types of compounds, it is necessary that the carbonyl and the chiral groups exist at nearby positions. Transition temperatures to those isotropic state for compounds **5** were lower than those for compounds **6**. This result is common in both cases of (+)-4-alkoxycarbonylphenyl-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]benzoates (**7**), and (+)-4-(2-methylbutoxy-carbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)-benzoates (**8**).

1. Introduction

As new types of nematic liquid crystal materials, some 2,5-disubstituted-1,3-dioxanes, -1,3-oxathianes, and -1,3-dithianes have been reported [1–18]. Recently, new types of liquid crystal displays using ferroelectric liquid crystals have been reported due to their shorter response time. Accordingly, various optically active compounds with the 1,3-dioxane, 1,3-oxathiane, or 1,3-dithiane ring have been synthesized [19–27]. In previous papers [20, 22], we have reported (+)-4-(2-methylbutoxycarbonyl)phenyl 4-(5-alkyl-1,3-dioxan-2-yl)benzoate (**8**), and (+)-4-(5-alkyl-1,3-dioxan-2-yl)phenyl] 4-(2-methylbutoxy)benzoates (**6**) as new materials exhibiting ferroelectric behaviour. The title compounds have the chemical structures in which the two terminal groups of compound **6** were exchanged. In this paper, we wish to report the synthesis of the title compounds and the chemical structural factors which influence the mesomorphic behaviour of these 1,3-dioxanes.

2. Experimental

IR, ^{1}H NMR, and mass spectra (MS) were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80 B spectrometer, respectively. Elemental analyses were carried out with a Perkin–Elmer 250 instrument. Transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro melting point apparatus equipped with polarizers and a Rigaku Denki DSC CN805Li, CN8208A2, respectively.

2.1. *4'-Formylphenyl 4-alkoxybenzoates* (*3*)

To a solution of compound **2** (0·015 mol) and 1,8-diazabi-cyclo[5.4.0]undec-7-ene (0·015 mol) in anhydrous *N*,*N*-dimethyl-formamide (30 ml) was added **1** (0·015 mol) in a

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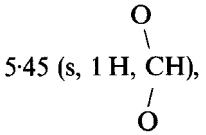
nitrogen atmosphere, followed by stirring at 40°C for 18 h. The solution was poured into ice water and shaken twice with ether (each 200 ml). The extract was washed with cold 5 per cent aqueous hydrochloric acid, dried over anhydrous sodium sulphate, and evaporated *in vacuo* at 40°C. The residue was extracted with hexane, and the extract concentrated under reduced pressure. The residue was purified by recrystallization from hexane and then by column chromatography. The white powder was obtained in 40–50 per cent. MP: $R=C_8H_{17}$, 65–67°C; $C_{10}H_{21}$, 85–87°C; $C_{11}H_{23}$, 97–100°C; $C_{12}H_{25}$, 115–118°C. IR ($CHCl_3$): 2800–3000 (alkyl), 1720, 1680 (C=O), 1600 (Ar), 1290 (ether) cm^{-1}. ^1H NMR ($CDCl_3$): δ0·7–2·2 (m, OCH_2R), 4·0 (t, 2 H, OCH_2), 6·8–8·2 (m, 8 H, ArH), 10·0 (s, 1 H, CHO).

2.2. (+)-*4'*-[*5*-(*2-methylbutyl*)-*1,3-dioxane-2-yl*]*phenyl 4-alkoxybenzoates* (*5*)

To a solution of compounds **4** (0·004 mol) and **3** (0·004 mol) in anhydrous $CHCl_3$ (200 ml), cooled in an ice bath were added $BF_3(C_2H_5)_2O$ (0·5 g) and molecular sieves (3 Å, 1/15; 3 g). The mixture was stirred at 0–5°C for 8 h and then at 20–25°C for 10 h. The solution was washed with 10 per cent aqueous $NaHCO_3$ (400 ml), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure at 40°C. The crude product was purified by column chromatography and recrystallized from hexane, followed by preparative thin layer chromatography (silica gel) to remove *cis* isomer. A white powder was obtained. IR ($CHCl_3$): 2800–3000 (alkyl), 1730 (C=O), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$): 0·7–2·3 (m, R'CH, OCH_2R), 3·3–4·5 (m, 6 H, OCH_2),

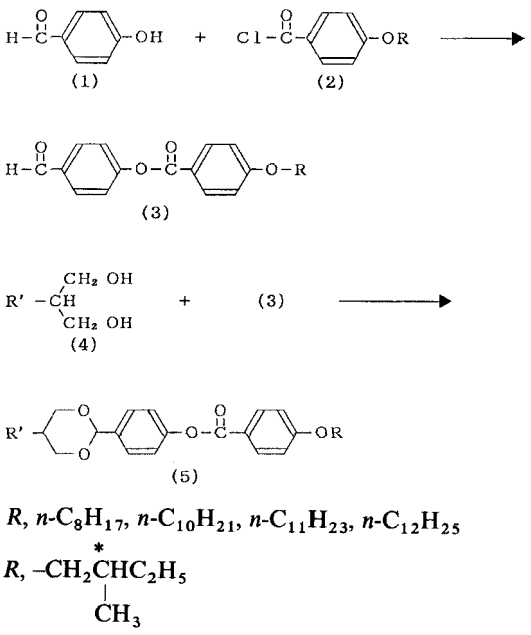


6·8–8·2 (m, 8 H, ArH). 5-1: yield, 36 per cent. $C_{30}H_{42}O_5$: found C 74·10 per cent H 8·84 per cent, calculated C 74·65 per cent, H 8·77 per cent. MS M^+ 482. 5-2: yield, 39 per cent. $C_{32}H_{46}O_5$: found C 75·05 per cent, H 9·11 per cent, calculated C 75·26 per cent, H 9·08 per cent. MS M^+ 510. 5-3: yield, 29 per cent. $C_{33}H_{48}O_5$: found C 75·25 per cent, H 9·25 per cent, calculated C 75·53 per cent, H 9·22 per cent. MS M^+ 524. 5-4: yield, 23 per cent. $C_{34}H_{50}O_5$: found C 76·01 per cent, H 9·32 per cent, calculated C 75·80 per cent, H 9·36 per cent. MS M^+ 538.

3. Results and discussion

The (+)-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]phenyl 4-alkoxybenzoates (**5**) were synthesized by the route shown in the scheme. Compounds **2** were synthesized through the three steps from ethyl 4-hydroxybenzoate.

Compounds **3** could be purified by recrystallization from hexane, then by column chromatography using benzene as eluant. Compound **4** was synthesized by two steps from (*S*)-(+)-1-bromo-2-methylbutane (purity 99 per cent; $n_D=1·444$) and diethylmalonate. Although compounds **5** were synthesized by the ring formation reaction of compounds **4** and **3**, in this step, both *trans* and *cis* isomers were produced. Hence, about five recrystallizations were needed to purify the *trans* isomer. In case the *cis* isomer could not be removed by recrystallization, preparative thin-layer chromatography was used to obtain the *trans* isomer. The ^1H NMR spectrum data for compounds **5** showed the C-2 proton signals for the 1,3-dioxane ring of the *trans* and *cis* isomers at $\delta=5·45$ and 5·50, respectively. Therefore, the removal of the *cis* isomer can be checked by the disappearance of the *cis* isomer's peak.



R, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{11}H_{23}$, n-$C_{12}H_{25}$

R, $-CH_2\overset{*}{C}HC_2H_5$ (with CH_3 branch)

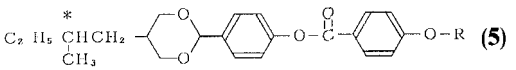
Synthetic pathway for the (+)-4-[5-(2-methylbutyl)-1,3-dioxan-2-yl]phenyl 4-alkoxybenzoates (**5**).

Measurements of the transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers. Phase identification was made by comparing the observed textures with those in the literature [28, 29]. Phase transition temperatures for compounds **5** and the corresponding compounds **6**, **7**, and **8** are given in the table. Although compounds **6** exhibited the chiral smectic C (S_C^*) phase, compounds **5** did not.

Compounds **5** have chemical structures in which two terminal substituents of compounds **6** are exchanged. The major difference between the chemical structures of compounds **5** and **6** is that the chiral alkoxy group is conjugated with the carbonyl group in compound **6**, but not in compound **5**. In this way, to exhibit the S_C^* phase it might be important that the chiral and the carbonyl groups are positioned near each other. The phase transition data of compounds **7** and **8** also support this conclusion. That is, compounds **8** having the chiral and the carbonyl groups at nearby positions exhibit the S_C^* phase, whereas compounds **7** having them apart do not. Therefore, in this type of 1,3-dioxane liquid crystal compound, the nearby-location of the chiral and the carbonyl groups seems to be necessary for the appearance of the S_C^* phase.

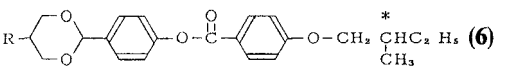
The transition temperatures to the isotropic state for compounds **5** and **7** are lower than those for the corresponding compounds **6** and **8**, respectively. In compounds **5** and **7**, the 2-methylbutyl group is at the C-5 carbon position of the 1,3-dioxane ring. As the 2-methylbutyl group and the 1,3-dioxane ring of compounds **5** and **7** are considered to hinder each other other sterically, judging from results obtained with molecular models. This may cause the greater molecular width of compounds **5** and **7**. Therefore, transition temperatures to the isotropic state for compounds **5** and **7** are lower than those for the corresponding compounds **6** and **8** respectively.

Table 1. Phase transition temperatures for compounds **5**, **6**, **7**, and **8**.



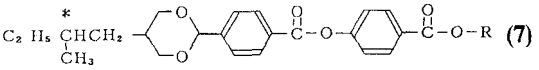
(5)

	R	Phase transition temperatures†
5–1	n-C_8H_{17}	C $\underset{38°C}{\overset{72°C}{\rightleftarrows}}$ Ch $\underset{124°C}{\overset{124°C}{\rightleftarrows}}$ I
5–2	n-$C_{10}H_{21}$	C $\underset{55°C}{\overset{75°C}{\rightleftarrows}}$ Ch $\underset{120°C}{\overset{120°C}{\rightleftarrows}}$ I
5–3	n-$C_{11}H_{23}$	C $\underset{70°C}{\overset{80°C}{\rightleftarrows}}$ Ch $\underset{119°C}{\overset{119°C}{\rightleftarrows}}$ I
5–4	n-$C_{12}H_{25}$	C $\underset{87°C}{\overset{87°C}{\rightleftarrows}}$ Ch $\underset{117°C}{\overset{117°C}{\rightleftarrows}}$ I



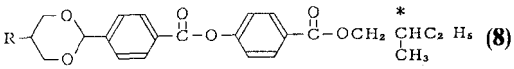
(6)

	R	Phase transition temperatures†
6–1	n-$C_{10}H_{21}$	C $\overset{69°C}{\rightarrow}$ Ch $\overset{123°C}{\rightleftarrows}$ I; C $\overset{40°C}{\uparrow}$ S_B $\underset{51°C}{\rightleftarrows}$ S_C^*; Ch $\underset{58°C}{\updownarrow}$ S_C^*
6–2	n-$C_{11}H_{23}$	C $\overset{76°C}{\rightarrow}$ Ch $\overset{124°C}{\rightleftarrows}$ I; C $\overset{35°C}{\uparrow}$ S_B $\underset{61°C}{\rightleftarrows}$ S_C^*; Ch $\underset{63°C}{\updownarrow}$ S_C^*
6–3	n-$C_{12}H_{25}$	C $\overset{82°C}{\rightarrow}$ Ch $\overset{118°C}{\rightleftarrows}$ I; C $\overset{30°C}{\uparrow}$ S_B $\underset{65°C}{\rightleftarrows}$ S_C^*; Ch $\underset{68°C}{\updownarrow}$ S_C^*



(7)

	R	Phase transition temperatures†
7–1	n-C_8H_{17}	C $\xrightarrow{74°C}$ I; C $\xrightarrow{50°C}$ Ch; Ch $\xrightarrow{66°C}$ I
7–2	n-$C_{10}H_{21}$	C $\underset{48°C}{\overset{67°C}{\rightleftarrows}}$ Ch $\underset{81°C}{\overset{81°C}{\rightleftarrows}}$ I
7–3	n-$C_{11}H_{23}$	C $\underset{51°C}{\overset{68°C}{\rightleftarrows}}$ Ch $\underset{76°C}{\overset{76°C}{\rightleftarrows}}$ I
7–4	n-$C_{12}H_{25}$	C $\xrightarrow{68°C}$ I; C $\xrightarrow{48°C}$ S_A; $S_A \underset{61°C}{\rightleftarrows}$ Ch; Ch $\xrightarrow{66°C}$ I



(8)

	R	Phase transition temperatures†
8–1	n-C_8H_{17}	C $\underset{27°C}{\overset{51°C}{\rightleftarrows}}$ S_C^* $\underset{69°C}{\overset{69°C}{\rightleftarrows}}$ S_A $\underset{141°C}{\overset{141°C}{\rightleftarrows}}$ I
8–2	n-$C_{10}H_{21}$	C $\underset{14°C}{\overset{59°C}{\rightleftarrows}}$ S_C^* $\underset{93°C}{\overset{93°C}{\rightleftarrows}}$ S_A $\underset{137°C}{\overset{137°C}{\rightleftarrows}}$ I
8–3	n-$C_{11}H_{23}$	C $\underset{-4°C}{\overset{62°C}{\rightleftarrows}}$ S_C^* $\underset{94°C}{\overset{94°C}{\rightleftarrows}}$ S_A $\underset{136°C}{\overset{136°C}{\rightleftarrows}}$ I
8–4	n-$C_{12}H_{25}$	C $\underset{30°C}{\overset{66°C}{\rightleftarrows}}$ S_C^* $\underset{95°C}{\overset{95°C}{\rightleftarrows}}$ S_A $\underset{135°C}{\overset{135°C}{\rightleftarrows}}$ I

† C, crystal; S, smectic; Ch, cholesteric; I, isotropic.

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