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Synthesis and Properties of Phenyl Cyclohexyl Ferroelectric Liquid Crystals

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In this work, twelve compounds: *S*(+)-4-[(2-methylbutyloxycarbonyl)phenyl]4′-(4″-trans-n-alkylcyclohexyl)benzoates; *S*(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-alkylcyclohexyl)benzoates, where alkyl $= C_5$—C_{10}, were synthesized. The effect of the alkyl chains on liquid crystal transition temperatures of two homologous series prepared has been investigated systematically. The mesomorphic properties are studied by DSC and Polarizing Microscopy. Chiral smectic C and chiral nematic mesophases, as well as a smectic A mesophase, in several cases, were observed.

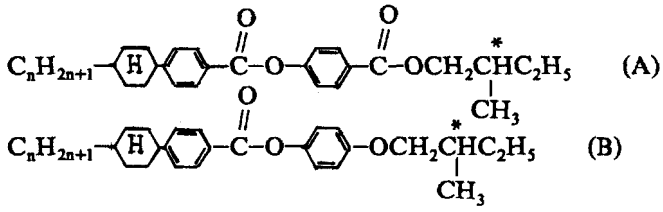
Keywords: ferroelectric liquid crystal, chiral smectic C, phenyl cyclohexyl liquid crystal

INTRODUCTION

Meyer et al.[1] have shown in 1975 that chiral compounds in the smectic C phase can exhibit a spontaneous polarization (P_s) and that these phases are ferroelectric; so it is possible to correlate the polarization with an external field, and in 1980, a new ferroelectric smectic device structure, the Surface Stabilized Ferroelectric Liquid Crystal structure (SSFLC) was reported.[2,3] SSFLC devices show high speed, bistability, a well defined threshold, and a large optical effect. Since then much attention has been given to the synthesis of new ferroelectric liquid crystals which show the following properties: (1) the chiral smectic C and the smectic A mesophases over a wide temperature range[4,5]; (2) large spontaneous polarization (P_s); (3) negative dielectric anisotropy; (4) small birefringence; (5) low rotating viscosity.[6–8] No single compound can satisfy all these specifications simultaneously, so mixtures of suitable components are needed.

It is well known that phenyl cyclohexyl liquid crystals have not only chemical, thermal, photo and electrochemical stability but also low melting point, low vis-

cosity.[9–11] From this point of view, we have synthesized the following series of compounds.



(A)

(B)

(n = 5–10)

RESULTS AND DISCUSSION

The phase sequence and transition temperatures of the synthesized compounds are given in Table I and Table II. Phase identification was done by comparing the observed textures with those found in the literature.[12,13]

TABLE I

Transition temperature (°C) of the series A

C_5H_{11}	K	91	S_C^*	135.5	N^*	153	I
C_6H_{13}	K	90	S_C^*	136	N^*	147	I
C_7H_{15}	K	82	S_C^*	137.5	N^*	148	I
C_8H_{17}	K	81	S_C^*	136	N^*	144	I
C_9H_{19}	K	75	S_C^*	137	N^*	143	I
$C_{10}H_{21}$	K	77	S_C^*	134	N^*	136	I

TABLE II

Transition temperatures (°C) of the series B

C_5H_{11}	K	73	S_C^*	110.5	S_A	148.5	N^*	160.5	I
C_6H_{13}	K	80	S_C^*	114	S_A	149.5	N^*	154	I
C_7H_{15}	K	80.5	S_C^*	120	S_A	153	N^*	154	I
C_8H_{17}	K	79	S_C^*	119	S_A	148	N^*	—	I
C_9H_{19}	K	69.5	S_C^*	125	S_A	150	N^*	—	I
$C_{10}H_{21}$	K	70.5	S_C^*	120	S_A	143	N^*	—	I

K: crystal, S: smectic, N^*: cholesteric

I: isotropic.

The dependence of transition temperatures on chain length of alkyl residue of the series A is given in Figure 1. The transition temperatures exhibit a general tendency to decrease with the increase of chain length, but the transition temperatures of the $S_c^* - N^*$ show little variation. The range of the S_c^* mesophase increases as the number of alkyl carbon atoms increases, on the contrary, the range of the N^* mesophase tends to decrease with increasing chain length. Figure 2 shows a plot of the melting ($K - S_c^*$), $T(S_c^* - S_A)$, $T(S_A - N^*$, or I) and $T(N^* - I)$ values as a function of the length of the terminal alkyl chain of the series B. Four curves are obtained; the odd and even alternation effect is apparent. The $T(K - S_c^*)$ curve is irregular. The curves of $T(S_c^* - S_A)$ and $T(S_A - N^*)$, or $T(S_A - I)$ increase from $n = 5$ to $n = 7$, then both curves show a normal pattern of alternation from $n = 7$ to $n = 10$. The shape of $T(N^* - I)$ curve shows a descent from $n = 5$ to $n = 7$.

It is noted that mesophase N^* disappears when the number of alkyl carbon atoms is equal to eight ($n = 8$).

Figures 3–6 show the textures of $S(+)$-4-[(2-methylbutyloxy carbonyl)phenyl] 4′-(trans-4″-n-pentylcyclohexyl)benzoate, 5A.

Figures 7–10 give the textures of $S(+)$-4-[(2-methylbutyloxy carbonyl)phenyl] 4′-(trans-4″-n-heptylcyclohexyl)benzoate, 7A.

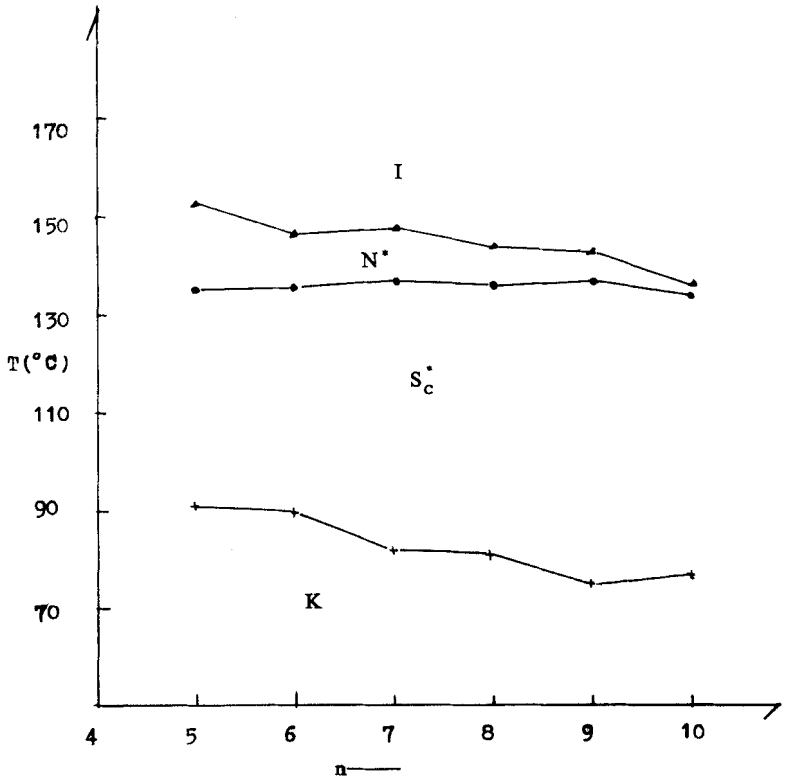


FIGURE 1 Plot of transition temperatures against the number of carbon atoms in the n-alkyl chain for the series A.

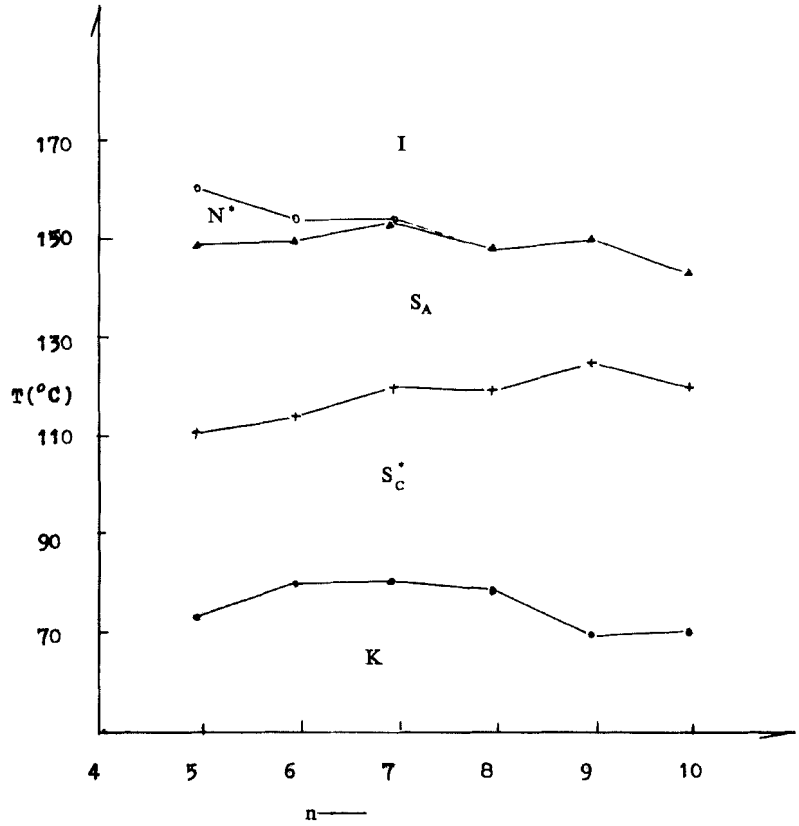


FIGURE 2 Plot of transition temperatures against the number of carbon atoms in the n-alkyl chain for the series B.

Figures 11–13 are the textures of *S*(+)-4-[(2-methylbutyloxy)phenyl]4′-(trans-4″-n-pentylcyclohexyl)benzoate, 5B.

CONCLUSION

Two new classes of ferroelectric liquid crystals have been prepared. The series A and B generally exhibit a wide range (45°C, on average) enantiotropic chiral smectic C and chiral nematic mesophase. Series B also exhibits enantiotropic smectic A mesophase over a wide range. For alignment of the ferroelectric liquid crystals and device fabrication, the four-phase sequence of the series B is considered important.[14]

EXPERIMENTAL PART

^{1}H-NMR: Varian. 90 MHz EM-390. IR: Perkin Elmer PE 257. Specific Optical rotation: Automatic polarimeter, WZZ-1S Shanghai China.

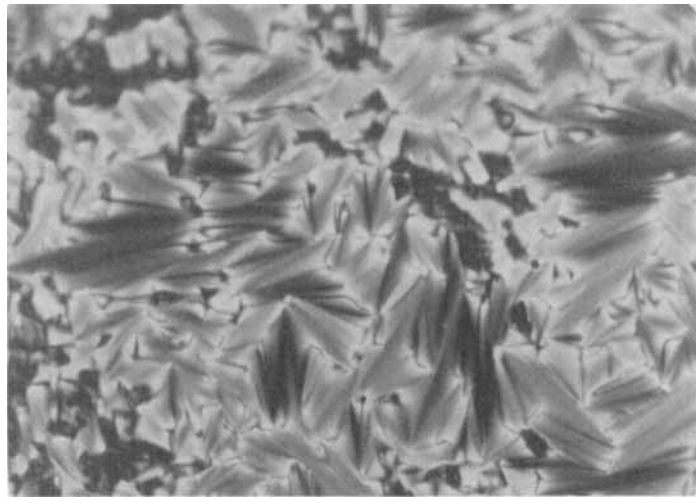


FIGURE 3 S_c^*, Simultaneous occurrence of schlieren and fan-shaped texture. Crossed polarizers, 104.5°C, X400. 5A. See Color Plate IV.

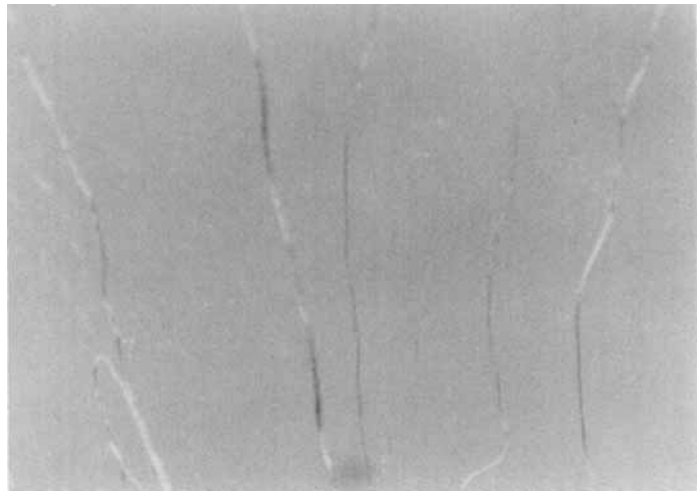


FIGURE 4 N^*, Cholesteric texture with oily streaks. Crossed polarizers, 136.5°C, X100. 5A. See Color Plate V.

Texture observation: Olympus polarizing microscope in conjunction with Olympus photomicrographic system PM-10AD and Newport heating stage model 871. Phase transition temperatures were determined by using DU PONT 990. Chromatographic purification was performed by using SP8800 ternary HPLC Pump and SP 8450 un/vis Detector. Elemental analysis: PE 240 C

S(−)-2-methylbutanol (95%), Fluka.

S(+)-4-[(2-methylbutyloxycarbonyl)phenyl]4′-(trans-4″-n-pentylcyclohexyl) benzoate, (n = 5), 5A. 4-(trans-4′-n-pentylcyclohexyl)benzoic acid (2.7 g, 0.01 m) was refluxed for 3 h with thionyl chloride (15 ml), excess $SOCl_2$ was evaporated

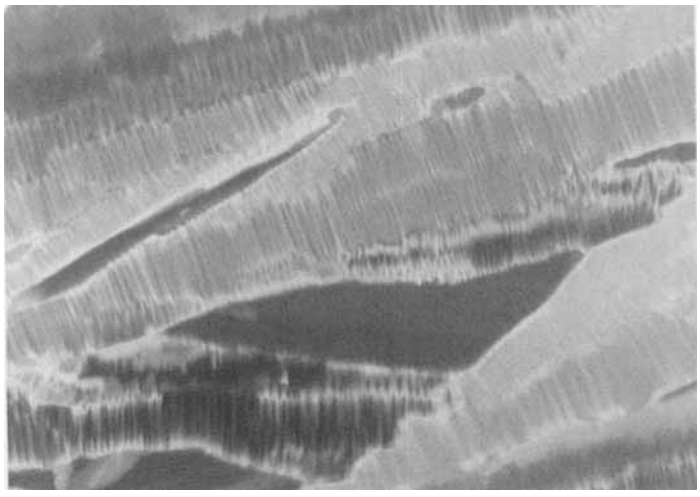


FIGURE 5 S_c^*, Domain texture. Crossed polarizers 131.4°C, X400. 5A. See Color Plate VI.

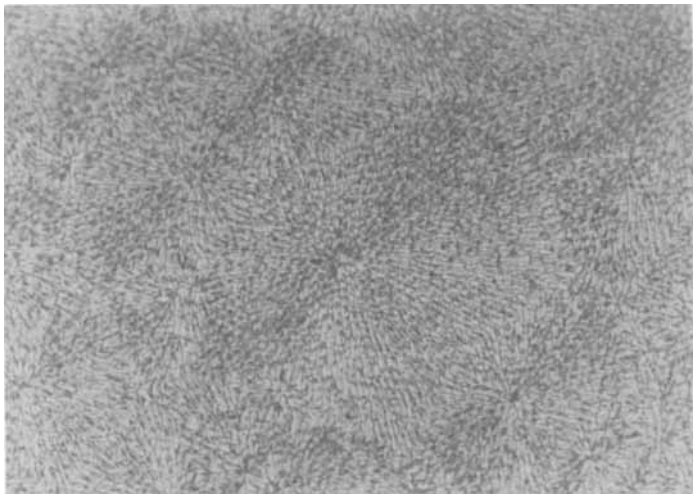


FIGURE 6 N^*, Cholesteric texture. Crossed polarizers, 146.5°C, X100. 5A. See Color Plate VII.

and the crude acid chloride was added to a solution of $S(+)$-(2-methylbutyloxy)4′-hydroxybenzoate (2.1 g, 0.01 m) in pyridine (15 ml). After stirring for 8 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 sulphate. The solvent was evaporated and the residue was recrystallized from ethanol to give pure 97.5%, white crystal (4.2 g, 75%). $[\alpha]_D^{25} = +8.73$ (c = 1.0, $CHCl_3$). ^{1}H NMR: δ 8.15(dd,J = 9 Hz, 4H)7.36(dd,J = 9 Hz,4H)4.24 (dd,J = 5.6 Hz, J = 3 Hz,2H) 2.6(m,1H) 1.96(m,10H) 1.0–1.6(m,19H) IR: (KBr, film) 3030 2930 2870 1740 1713 1630 1270 1025 775 cm^{-1}. Calcd. for $C_{30}H_{40}O_4$ C 77.54; H 8.68, found: C 77.58; H 8.66.

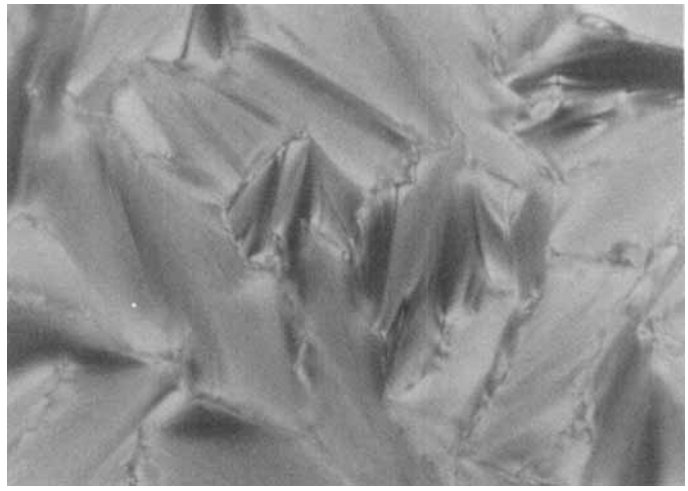


FIGURE 7 S_c^*, broken fan-shaped texture. Crossed polarizers, 133°C, X400. 7A. See Color Plate VIII.

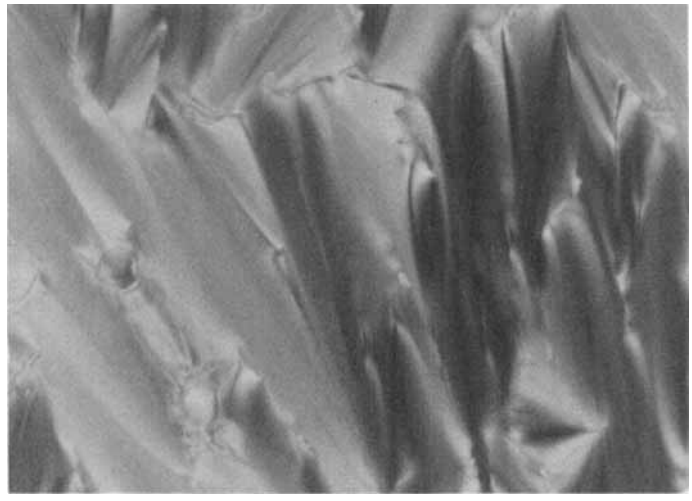


FIGURE 8 S_c^*, broken fan-shaped texture. Crossed polarizers, 132°C, X400. 7A. See Color Plate IX.

The following esters were prepared by using the same procedure:

$S(+)$ - 4 - [(2 - methylbutyloxycarbonyl)phenyl]4′ - (trans - 4″ - n - hexylcyclohexyl) benzoate, yield 76%; pure 95.5%. $[\alpha]_D^{25} = +13.13$ ($c = 1.0$, $CHCl_3$). Calcd. for $C_{31}H_{42}O_4$ C 77.78, H 8.84, found: C 78.02; H 8.87.

$S(+)$ - 4 - [(2 - methylbutyloxycarbonyl)phenyl]4′ - (trans - 4″ - n - heptylcyclohexyl) benzoate, 7A, yield 78%, pure 98%; $[\alpha]_D^{25} = +17.01$ ($c = 1.0$, $CHCl_3$). Calcd. for $C_{32}H_{44}O_4$ C 78.00; H 9.00, found: C 77.26; H 8.90.

$S(+)$ - 4 - [(2 - methylbutyloxycarbonyl)phenyl]4′ - (trans - 4″ - n - octylcyclohexyl) benzoate, yield 71%; pure 96.5%; $[\alpha]_D^{25} = +7.95$ ($c = 1.0$, $CHCl_3$). Calcd. for $C_{33}H_{46}O_4$ C 78.22; H 9.15, found: C 78.09; H 9.23.

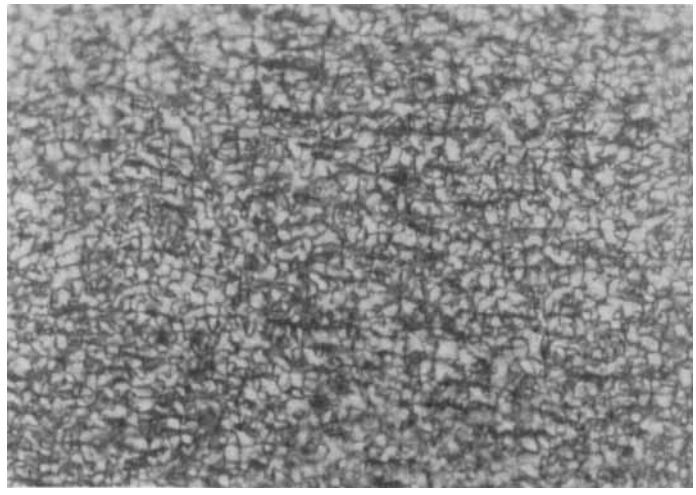


FIGURE 9 N^*, schlieren texture. Crossed polarizers, 143°C, X400. 7A. See Color Plate X.

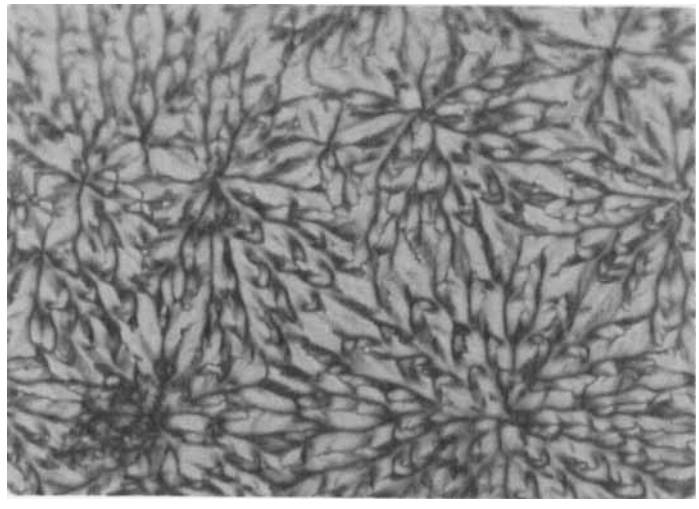


FIGURE 10 N^*, cholesteric texture. Crossed polarizers, 147.1°C, X400. 7A. See Color Plate XI.

$S(+)$-4-[(2-methylbutyloxycarbonyl)phenyl]-4′-(trans-4″-n-nonylcyclohexyl) benzoate, yield 73%; pure 97%; $[\alpha]_D^{25} = +9.11$ ($c = 1.0$, $CHCl_3$). Calcd. for $C_{34}H_{48}O_4$ C 78.42; H 9.29, found: C 77.82; H 9.27.
$S(+)$-4-[(2-methylbutyloxycarbonyl)phenyl]-4′-(trans-4″-n-decylcyclohexyl) benzoate, yield 72%; pure 96.5%; $[\alpha]_D^{25} = +8.77$ ($c = 1.0$, $CHCl_3$). Calcd. for $C_{35}H_{50}O_4$ C 78.60; H 9.41, found: c 77.93; H 9.42.
$S(+)$-4-[(2-methylbutyloxy)phenyl[4′-(4″-trans-n-pentylcyclohexyl)benzoate, ($n = 5$), 5B. A solution of 4-(trans-4′-n-pentylcyclohexyl)benzoic acid (2.7 g, 0.01 m) was refluxed for 3 h with thionyl chloride (15 ml), excess $SOCl_2$ was evaporated

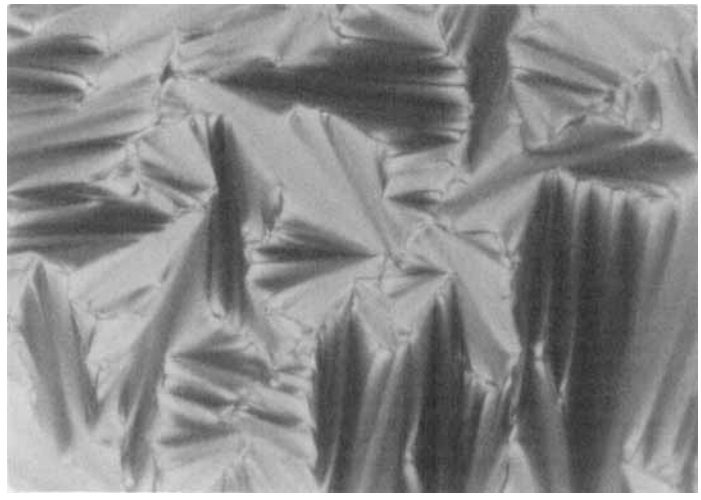


FIGURE 11 S_c^*, broken fan-shaped texture. Crossed polarizers, 108.2°C, X400. 5B. See Color Plate XII.

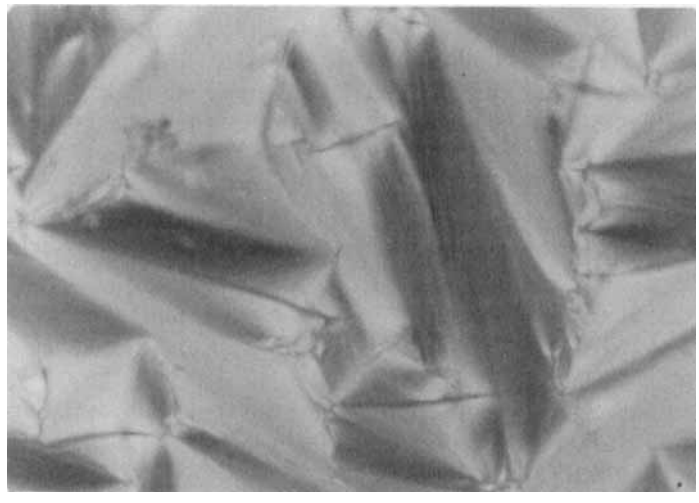


FIGURE 12 S_A, fan-shaped texture. Crossed polarizers, 145°C, X400. 5B. See Color Plate XIII.

and the crude acid chloride was added to a solution of 4-(2′-methylbutyloxy)phenol (1.8 g, 0.01 m) in benzene (20 ml) containing pyridine (4 ml). The mixture was refluxed in boiling benzene for 3 h, the reaction mixture ws cooled down and poured into diluted hydrochloric acid. The organic phase was separated, washed with water and dried over magnesium sulphate, then the solvent was evaporated. The crude product was twice recrystallized from ethanol to yield pure (97%) white crystal (3.4 g, 80%). $[\alpha]_D^{25} = +12.29$ ($c = 1.0$, in $CHCl_3$). ^1H NMR: δ 8.16 (d,J = 8 Hz, 2H) 7.35 (d,J = 8 Hz, 2H) 7.16 (d,J = 9 Hz, 2H) 6.96 (d,J = 9 Hz, 2H) 3.88 (dd,J = 5.6 Hz, J = 3 Hz, 2H) 2.6 (m, 1H) 1.96 (m, 10 H) 1.0–1.6 (m, 19H)

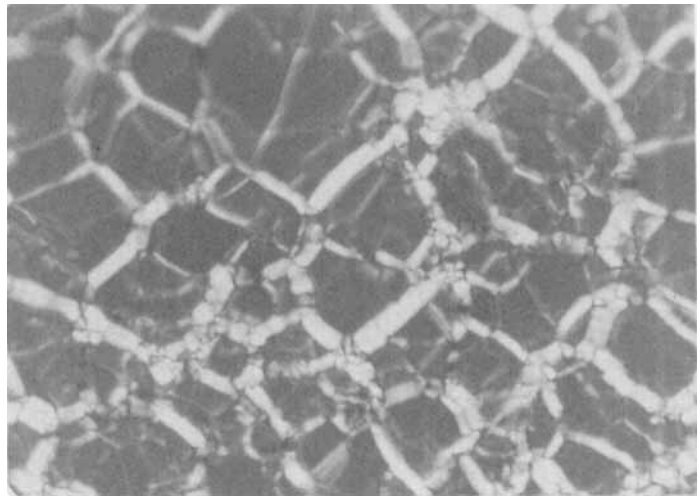


FIGURE 13 N^*, cholesteric texture with oily streaks. Crossed polarizers, 152°C, X400. 5B. See Color Plate XIV.

IR: (KBr, film) 3030, 2960, 2870, 1739, 1530, 1186, 1110, 833 cm^{-1}. Calcd. for $C_{29}H_{40}O_3$ C 79.77; H 9.23, found: C 79.51; H 9.44

The following ester could be prepared by the same method:

S(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-hexylcyclohexyl)benzoate, yield 83%, pure 96%; $[\alpha]_D^{25} = +14.19$ (c = 1.0, $CHCl_3$). Calcd. for $C_{30}H_{42}O_3$ C 79.95; H 9.39, found: C 80.45, H 9.41.

S(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-hexylcyclohexyl)benzoate, yield 85%; pure 96.5%; $[\alpha]_D^{25} = +16.93$ (c = 1.0, $CHCl_3$). Calcd. for $C_{31}H_{44}O_3$ C 80.13; H 9.54, found: C 80.04; H 9.45.

S(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-octylcyclohexyl)benzoate, yield 86%; pure 98%; $[\alpha]_D^{25} = +19.56$ (c = 1.0, $CHCl_3$). Calcd. for $C_{32}H_{46}O_3$ C 80.28; H 9.68, found: C 79.96; H 9.61.

S(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-hexylcyclohexyl)benzoate, yield 85%; pure 97%; $[\alpha]_D^{25} = +12.08$ (c = 1.0, in $CHCl_3$). Calcd. for $C_{33}H_{48}O_3$ C 80.41; H 9.82, found: C 80.09; H 9.79.

S(+)-4-[(2-methylbutyloxy)phenyl]4′-(4″-trans-n-decylcyclohexyl)benzoate, yield 84%; pure 98%; $[\alpha]_D^{25} = +9.50$ (c = 1.0, $CHCl_3$). Calcd. for $C_{34}H_{50}O_3$ C 80.58; H 9.94, found: C 80.73; H 9.97.

S(+)-4-[(2′-methylbutyloxy)phenol, *S*(+)-(2-methylbutyl)4′-hydroxybenzoate and 4-(trans-4′-n-alkylcyclohexyl)benzoic acids were prepared by the methods reported in the literatures.[15–17]

Acknowledgment

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