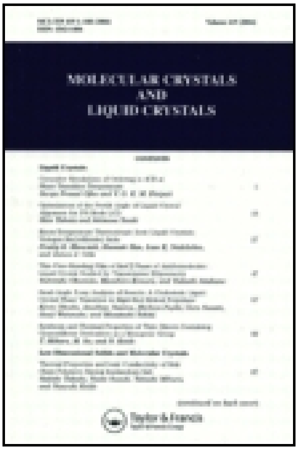

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Synthesis of Novel Ferroelectric Liquid Crystals Derived from L-tyrosine*

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A new series of ferroelectric liquid crystalline Schiff base compounds with the general formula, 4-(*p*-butyloxy-2-chloro-tyrosinate)2-hydroxy-benzylidene-4′-alkylanilines (BCTHBA) using L-tyrosine as a chiral source have been synthesized and characterized by elemental analyses, IR and PMR spectral techniques. The liquid crystalline properties *viz.*, textural identification, the phase transition temperatures and ferroelectricity were studied by thermal microscopy, differential scanning calorimetry and spontaneous polarization (by triangular wave method) techniques, respectively.

Keywords: BCTHBA; ferroelectric liquid crystal; smectic-C*; spontaneous polarization

INTRODUCTION

Since the first high speed electrooptic device based on a ferroelectric liquid crystal (FLC) was discovered [1], a great interest has been directed towards the search for new FLC materials to satisfy future application demands. Spontaneous polarization (P_s) is one of the important physical properties of FLC materials that ensure high switching speed. The last decade has witnessed a number of FLC compounds with extremely large spontaneous polarization utilizing amino acids as the chiral source [2]. In quest of high spontaneous polarized materials, we have made an attempt to synthesize a

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new series of FLC compounds derived from L-tyrosine and the molecular skeleton of BCTHBA (Fig. 1) has been designed in such a wat that: (a) a highly electronegative atom (Cl) was substituted at the chiral carbon which enhances the high dipole moment (b) the distance between the chiral carbon and the core carbon was minimized and (c) an —OH group was substituted at the ortho position of the benzylidene moiety, initiating intra-molecular H-bonding with imine nitrogen thereby restricting the free rotation of the molecule along the long axis.

EXPERIMENTAL

The synthetic route along with the reaction conditions are shown in Scheme 1. The chiral centre introduced in these compounds was isolated from the corresponding L-tyrosine, available commercially in high enantiomeric purity. The α-chloro acid was synthesized by means of nucleophilic substitution of the $-NH_2$ group by a chlorine atom *via* the diazonium salt, as reported by Fu *et al.* [3]. The substitution takes place with the retention of asymmetric configuration [4]. The intermediate compounds obtained during the synthesis were well characterized by ^1H NMR, IR and mass spectral analyses. All the isolated compounds of the present Schiff base series showed a high degree of stability at room temperature. This stability may be attributed to the presence of intra-molecular H-bonding between the oxygen at the ortho-position of the benzylidene ring and the nitrogen in the imine group [5].

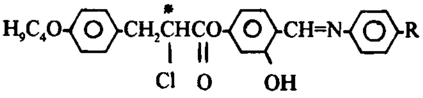
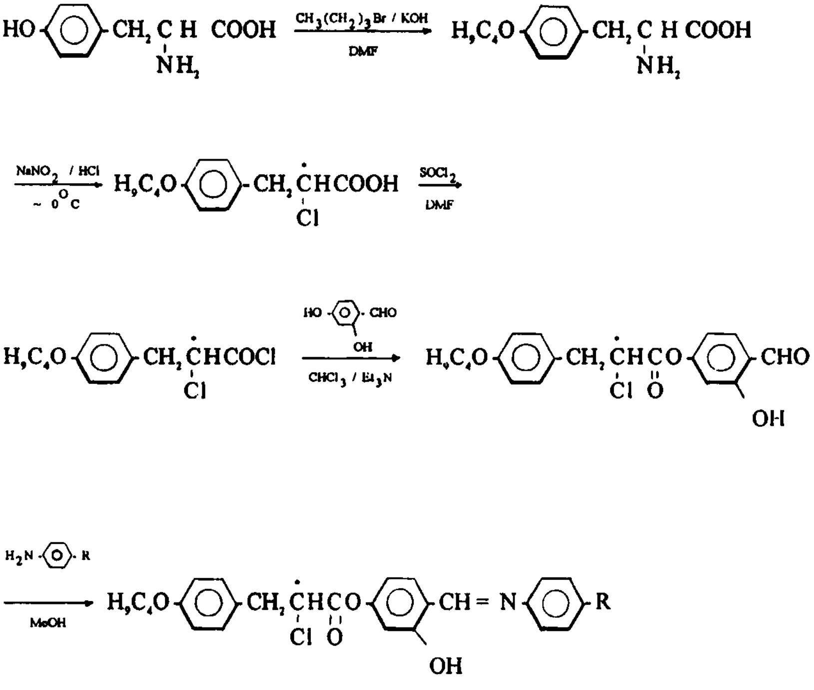


FIGURE 1 Structure of BCTHBA.

Compound	*R*
1	$-(CH_2)_4CH_3$
2	$-(CH_2)_6CH_3$
3	$-(CH_2)_8CH_3$
4	$-(CH_2)_{11}CH_3$
5	$-(CH_2)_{13}CH_3$



SCHEME 1

1-Bromobutane and 4-alkylanilines (99% purity) supplied by Aldrich Chemical Company, USA were used as such without further purification. The solvents used in the present study were purified by standard literature procedures [7]. The C, H and N microanalyses were carried out on a Perkin-Elmer 240C analyzer. Chlorine was estimated gravimetrically [8] as AgCl. The ^{1}H NMR spectra in $CDCl_3$ were run on a Jeol FX-90Q (90 MHz) multinuclear spectrometer. The solid state IR spectra were recorded (as KBr pellets) on a JASCO-5300 FT-IR spectrophotometer. The spontaneous polarization was measured in polyimide coated 10 μ cells (supplied by Display Tech, USA) by the field reversal method with a modified integrator part [9]. Textural observations were carried out *via* thermal microscopy with a Hertel-Reuss (Super pan-II) polarized microscope equipped with a PC monitored Instec (Boulder) mK heating stage. The preliminary phase transition temperatures recorded in cooling the isotropic liquid through the microscopic textures were accurate to ±0.1°C. The differential scanning thermograms were recorded on a Perkin-Elmer DSC-7 with a scanning rate of 5°C/min.

Alkylation of —OH group of L-tyrosine by 1-bromobutane

To a solution of L-tyrosine (5.43 g, 30 mmol) in 50 cm^3 DMF were added DMF solution (40 cm^3) of KOH (1.68 g, 30 mmol) and 1-bromobutane (4.11 g, 30 mmol). The resulting reaction mixture, stirred under reflux, yielded a yellow precipitate (as KBr) which was suction filtered and washed repeatedly with the solvent medium. The yellow resulting solution was extracted with diethyl ether and dried over sodium sulphate for ~ 12 h. The yellow oil product of *p*-butoxytyrosine with 78.5% yield was obtained by removing the excess ether by distillation under reduced pressure.

Incorporation of chiral centre on the α-carbon of L-tyrosine

An amount of 5.92 g (25 mmol) of *p*-butoxytyrosine was dissolved in 50 cm^3 of 6N HCl and the solution was brought to ~ 0°C. The resultant solution was stirred vigorously and to it 2.41 g (35 mmol) of freshly pulverized sodium nitrate was added in small portions at such a rate that the temperature of the solution remained between 0°C and 5°C. The stirring was continued at ~ 2°C for ~ 8 h. The solution was then extracted with ether and the etherial layer was dried over anhydrous Na_2SO_4 for 12 h. The yellow α-chloro acid obtained on evaporating the excess ether was fractionally distilled twice.

Esterification of α-chloro acids

The esterification of α-chloro acids with 2,4-dihydroxybenzaldehyde was made *via* acid chloride in $CHCl_3/Et_3N$ with the retention of asymmetric configuration, as reported by Sierra *et al.* [5]. The corresponding acid chlorides were prepared by cooling the α-chloro acids to 10°C in DMF and adding a slight excess of chilled thionyl chloride solution and a few drops of phosphorous trichloride. The mixture was shaken vigorously in an ice bath at 10°C for ~ 2 h and the resulting homogeneous mixture was stirred under reflux for ~ 2.5 h. The excess solvent was removed by vacuum distillation to obtain a yield of 64%.

Synthesis of Schiff base

The Schiff bases were prepared by the condensation of absolute methanolic solutions of the corresponding chiral aldehydes with the alkyl anilines in equimolar ratio [5] and the yellow crystalline Schiff bases after recrystallizing from hot ethanol solution were further purified by passing through a silica gel column using a mixture of petroleum ether: acetone (5:1 v/v) as eluent to obtain a yield of 1.8 g.

RESULTS AND DISCUSSION

The phase variants and their transition temperatures (vide Tab. I) were determined [6] from the characteristic textural observations under a polarized microscope. The ferroelectric BCTHBA series of liquid crystal compounds (1 – 5) exhibited focal conic fan textures in the smectic-A phase, arced focal conic fan (with concentric striations) in the smectic-C* phase (Plate 1), while the smectic-C* to smectic-F* phase transition was identified by a broken focal conic texture. It has been observed that all the compounds exhibit considerable temperature ranges (~ 30°C) of the Sm C* phase. The general phase sequence of the present compounds can be represented as -

Iso---SmA---SmC*---SmF*---K

The thermal microscopic observations of the onset of ferroelectric SmC* phase and the measurement of spontaneous polarization (P_s) were carried out simultaneously. The spontaneous polarization in the Sm C* phase was found to increase with decreasing temperature. The temperature dependence of P_s for a representative case is given as Figure 2 (for compound-3 the P_s, ~ 5.0 nC/cm^2 at 77°C). The phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the DSC thermograms (Fig. 3) and the corresponding ΔH values were depicted in Table I.

TABLE I Phase transition temperatures# (in °C) of BCTHBA series from thermal microscopy and DSC*

Compound	*Iso. – A*		*A – C**		*C* – F**		*F* – K*	
	TM	*DSC*	*TM*	*DSC*	*TM*	*DSC*	*TM*	*DSC*
1	113	112.25 (10.39)	86	86.30 (0.66)	55	55.63 (4.41)	51	–
2	105.5	116.01 (9.34)	93.6	94.14 (0.48)	63	62.76 (2.98)	50	–
3	115	114.25 (13.07)	88.1	88.37 (0.51)	60	59.32 (5.66)	59	–
4	113.4	114.02 (9.95)	88	89.52 (0.38)	59.3	58.75 (5.45)	58	–
5	117.6	118.18 (14.54)	92.1	93.23 (0.68)	65	66.85 (6.81)	59	–

Phase transition temperatures observed in colling run;

* ΔH values (in J/g) are given in parentheses.

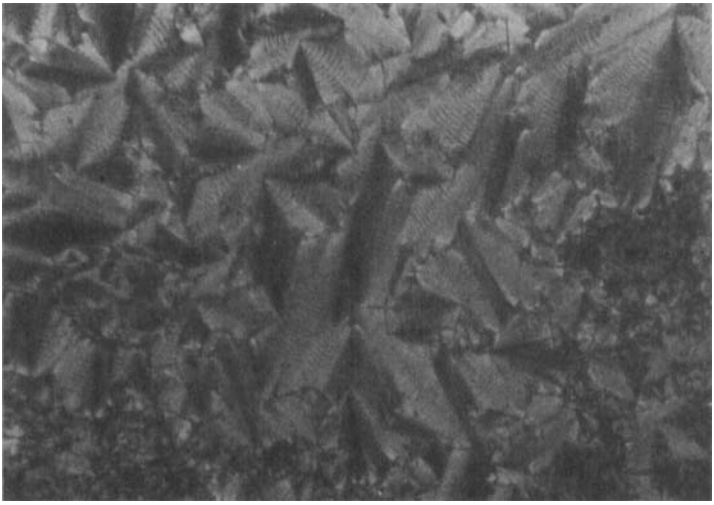


PLATE 1 Chiral Smectic-C* texture of compound-3. (See Color Plate IX).

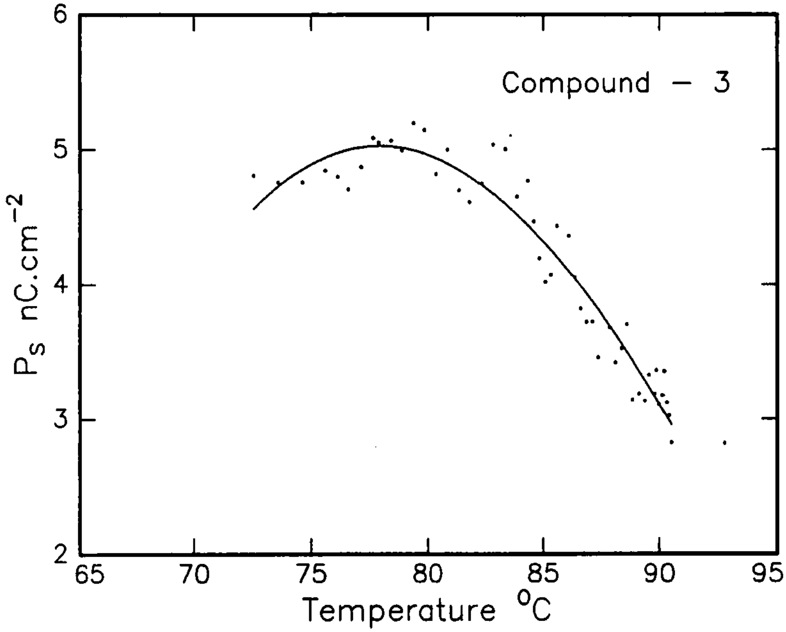


FIGURE 2 Temperature variation of spontaneous polarization in compound-3.

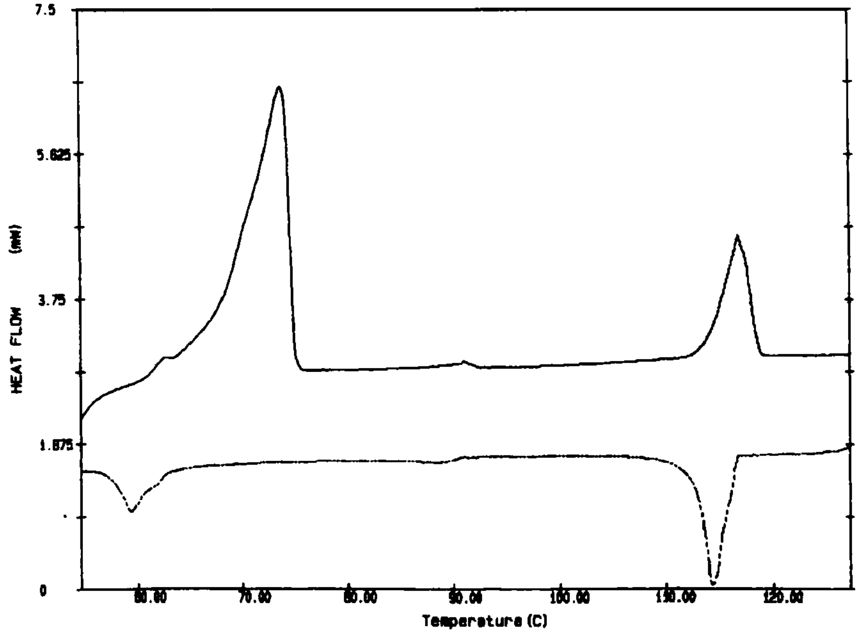


FIGURE 3 DSC thermogram for compound-3.

Characterization of the Compounds

Compound I

Elemental anal.cal. for $C_{31}H_{36}NO_4Cl$: C, 71.31%; H, 6.95%; N, 2.68%; Cl, 6.79%. Found: C, 71.29%; H, 6.91%, N, 2.71%; Cl, 7.02%. m.p. (clearing temp.) 114–116°C; Yield, 28%.

^{1}H NMR (δppm in $CDCl_3$) 1.12 (*t*, 6H, CH_3); 1.8–2.06 (*m*, 14H, CH_2); 3.84 (*t*, 1H, CH); 8.17 (*s*, 1H, NCH); 3.66 (*t*, 2H, OCH_2); 7.14 (*d*, 2H, Ph); 7.34 (*d*, 2H, Ph); 8.44–8.64 (*m*, 6H, Ph); 8.72 (*s*, 1H, Ph); 11.17 (*s*, 1H, OH); IR (cm^{-1} as KBr pellet) 1590, ν(CH=N); 1613, ν(C=O); 310, ν(CH—Cl); Mass spectrum: M^+ ion, 522.

Compound II

Elemental anal. cal. for $C_{33}H_{40}NO_4Cl$: C, 72.04%; H, 7.33%; N, 2.54%; Cl, 6.44%. Found: C, 72.12%; H, 7.28%; N, 2.51%; Cl, 6.78%. m.p. (clearing temp.) 110–112°C; Yield, 28%.

^{1}H NMR (δ ppm in $CDCl_3$) 1.16 (*t*, 6H, CH_3); 1.76–2.18 (*m*, 18H, CH_2); 3.78 (*t*, 1H, CH); 8.08 (*s*, 1H, NCH); 3.65 (*t*, 2H, OCH_2); 7.11 (*d*, 2H, Ph); 7.41 (*d*, 2H, Ph); 8.38–8.63 (*m*, 6H, Ph); 8.78 (*s*, 1H, Ph); 11.23 (*s*, 1H, OH) ; IR (cm^{-1} as KBr pellet) 1590, ν(CH=N); 1613, ν(C=O); 310, ν(CH—Cl); Mass spectrum: M$^+$ ion, 550.

Compound III

Elemental anal. cal. for $C_{35}H_{44}NO_4Cl$: C, 72.70%; H, 7.67%; N, 2.42%; Cl, 6.13%. Found: C, 72.72%; H, 7.64%; N, 2.41%; Cl, 6.04%. m.p. (clearing temp.) 108–110°C; Yield, 28%.

^{1}H NMR (δ ppm in $CDCl_3$) 1.2 (*t*, 6H, CH_3); 1.76–2.18 (*m*, 22H, CH_2); 3.73 (*t*, 1H, CH); 8.18 (*s*, 1H, NCH); 3.63 (*t*, 2H, OCH_2); 7.08 (*d*, 2H, Ph); 7.45 (*d*, 2H, Ph); 8.42–8.73 (*m*, 6H, Ph); 8.74 (*s*, 1H, Ph); 11.23 (*s*, 1H, OH); IR (cm^{-1} as KBr pellet) 1594, ν(CH=N); 1616, ν(C=O); 315, ν(CH—Cl); Mass spectrum: M$^+$ ion, 578.

Compound IV

Elemental anal. cal. for $C_{38}H_{50}NO_4Cl$: C, 73.58%; H, 8.12%; N, 2.25%; Cl, 5.71%. Found: C, 73.52%; H, 8.07%; N, 2.26%; Cl, 6.43%. m.p. (clearing temp.) 109–111°C; Yield, 28%.

^{1}H NMR (δ ppm in $CDCl_3$) 1.17 (*t*, 6H, CH_3); 1.74–2.23 (*m*, 28H, CH_2); 3.78 (*t*, 1H, CH); 9.03 (*s*, 1H, NCH); 3.55 (*t*, 2H, OCH_2); 7.14 (*d*, 2H, Ph); 7.42 (*d*, 2H, Ph); 8.3–8.67 (*m*, 6H, Ph); 8.78 (*s*, 1H, Ph); 11.16 (*s*, 1H, OH); IR (cm^{-1} as KBr pellet) 1589, ν(CH=N); 1611, ν(C=O); 315, ν(CH—Cl); Mass spectrum: M$^+$ ion, 620.

Compound V

Elemental anal. cal. for $C_{40}H_{54}NO_4Cl$: C, 74.10%; H, 8.39%; N, 2.16%; Cl, 5.47%. Found: C, 74.12%; H, 8.38%; N, 2.13%; Cl, 6.34%. m.p. (clearing temp.) 108–110°C; Yield, 28%.

^{1}H NMR (δ ppm in $CDCl_3$) 1.21 (*t*, 6H, CH_3); 1.76–2.64 (*m*, 32H, CH_2); 3.86 (*t*, 1H, CH); 8.78 (*s*, 1H, NCH); 3.67 (*t*, 2H, OCH_2); 6.97 (*d*, 2H, Ph); 7.71 (*d*, 2H, Ph); 8.08–8.54 (*m*, 6H, Ph); 8.78 (*s*, 1H, Ph); 10.11 (*s*, 1H, OH); IR (cm^{-1} as KBr pellet) 1598, ν(CH=N); 1614, ν(C=O); 315, ν(CH—Cl); Mass spectrum: M$^+$ ion, 648.

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