Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Manuel, L. R. , Cada, L. G. and Chien, L. C.(2005) 'Synthesis and physical properties of difluoroterphenyl ferroelectric liquid crystal with mixed alkenyloxy-ester terminal ends', Liquid Crystals, 32: 2, 163 — 172

To link to this Article: DOI: 10.1080/02678290412331327974

URL: http://dx.doi.org/10.1080/02678290412331327974

Liquid Crystals, Vol. 32, No. 2, February 2005, 163–172

Synthesis and physical properties of difluoroterphenyl ferroelectric liquid crystal with mixed alkenyloxy-ester terminal ends

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(*Received 2 June 2004; accepted 30 August 2004*)

This paper describes the synthesis and mesomorphic properties of a SmC*-forming liquid crystalline compound with potential display applications. This compound with two fluorines in the 3,3′-positions of the terphenyl core and mixed unsaturated alkoxy/ester terminal groups is synthesized in an attempt to obtain a liquid crystal with ferroelectric properties useful for display applications.

1. Introduction

The interest in the study of ferroelectric liquid crystals (FLCs) stem from two considerations. First is the technological importance: FLC compounds have good potentials as electroactive media that have varied uses in display technology. This technology has become a field of tremendous importance during recent decades, as illustrated by inventions of varied applications such as light valves, spatial light modulators, optical information processing and fast submicrosecond electro-optic switching [1, 2]. Secondly, and the more important reason for chemists to study FLCs, is they are relatively novel compared with nematic liquid crystals, therefore, many improvements in their physical/chemical properties can still be sought. In this regard, there has been much activity in the synthesis and structure–property relationships of these materials with the emphasis on optimizing specific properties for specific applications [3, 4].

The work presented in this paper consists of the design, synthesis and characterization of the ferroelectric liquid crystal *S*(+)-(2-octyl)-4″-decenyloxy-3,3′-difluoroterphenyl-4-carboxylate (see structure in figure 1; designated as compound **11**), with improved electro-optical properties suitable for display applications [5, 6]. Electro-optic results will be presented elsewhere. In this work, the chiral smectic C broken fan texture seen under a polarizing optical microscope is used as the basis for the presence of ferroelectricity.

2. Methodology

2.1. *Characterization*

Evaluation of features and physical properties was accomplished by the use of several spectroscopic techniques. Structures and chemical purities were confirmed by ^{1}H and ^{13}C NMR spectra using a 200 MHz Varian–Gemini NMR spectrometer, with $CDCl_3$ as solvent (unless otherwise stated in the text) and TMS as internal standard; and with a Nicolet Magna-FTIR 550 spectrophotometer.

Mesomorphic properties such as textures and transition temperatures were determined by polarizing optical microscopy using a Leitz Laborlux S polarizing microscope (magnification 200×) equipped with a Mettler FP52 hot stage, a Mettler FP5 control unit and a Wild Leitz MP552 camera in conjunction with a Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a TAC7/DX thermal analysis controller. Heating and cooling scan rates of $5.0^{\circ}\mathrm{C\,min^{-1}}$ were used. Transition temperatures are reported as the maxima and minima of their endothermic and exothermic peaks, respectively.

Optical rotations were determined with a Polyscience SR6 polarimeter using $CHCl_3$ as solvent.

2.2. *Materials*

All reagents and solvents were obtained from Sigma-Aldrich and were used without further purification, except for the THF used in the lithiation reaction, which was predistilled with Na metal under N_2 immediately before used. The reagents butyllithium in hexane, isopropyl borate, tetrakistriphenylphosphinepalladium(0)

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331327974

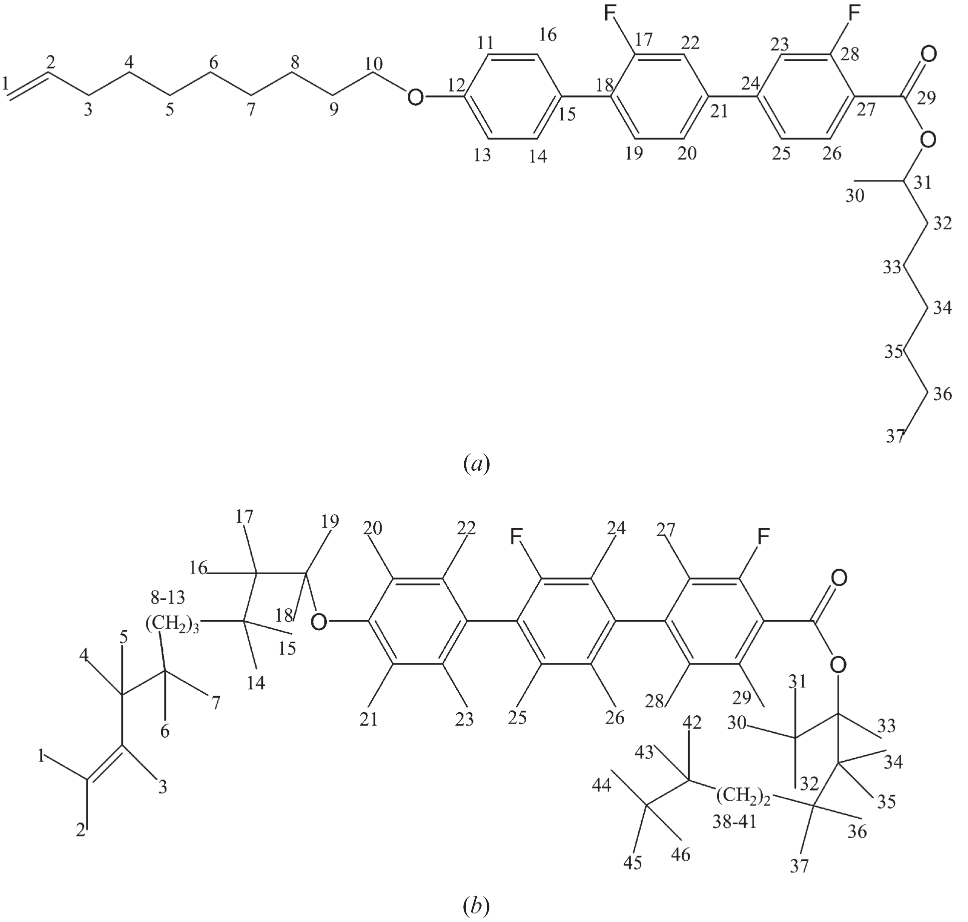

Figure 1. Structure of compound **11**. Numbers are for (*a*) ^{13}C NMR and (*b*) ^{1}H NMR peak assignments.

$Pd(PPh_3)_4$, diethylazodicarboxylate (DEAD) were stored in a refrigerator. Other reagents were used as received.

2.3. *Design of the compound*

Illustrated in figure 1, the compound under study has a 3,3′-difluorinated terphenyl core with mixed unsaturated alkoxy/ester terminal groups. Terphenyl cores are more popular over the biphenyls and quaterphenyls because of their higher optical anisotropy over the former and lower transition temperatures over the latter [7–9]. The two F-substituents at the 3,3′-positions are utilized to suppress the melting point of the potential ferroelectric liquid crystal close to the room temperature, with minimum increase in the viscosity. Other halogens are larger in size and therefore tend to produce more viscous liquid crystals [10]; high viscosity retards the electro-optic responses of liquid crystals.

Difluorinated systems with mixed alkyl/alkoxy terminal groups have been thoroughly studied, but not the 3,3′-position and mixed alkoxy/ester systems [9, 11, 12]. McDonnell *et al.* in 1995, in fact, correlated the formation of ferroelectric liquid crystal with the distance between the two lateral fluorines in the terphenyl cores. The group reported that the larger this distance, the larger is the possibility of the formation of a ferroelectric liquid crystal [13]. Trifluorination and tetrafluorination of such cores have also recently been reported [14–16].

The ester with its chiral branched centre as a terminal system is known to give lower transition temperatures compared with alkyl systems, thus again favouring use of the liquid crystal for display applications. This is due to weaker packing of ester molecules compared with the alkyls. The proximity of the chiral centre to the core also favours ferroelectricity as previous studies have shown. Furthermore, alkyl and alkoxy work together, with the proper orientation, to extend the aromatic content of the liquid crystal, thus further increasing birefringence and dielectric anisotropy [17–19]. The terminal vinyl moiety was introduced for further enhancement of ferroelectricity, in case the distance between the two lateral fluorines is not great enough to induce tilting and therefore ferroelectricity [20]. Finally, the lengths of the alkyl chains (both for the alkoxy and ester segments) can still be varied. The use of chain lengths of seven carbon atoms or even more than 10, may be examined in future work.

2.4. *Synthesis*

The synthetic scheme of the 11-step reaction to produce the ferroelectric liquid crystal, *S*(+)-(2-octyl) 4″-decenyloxy-3,3′-difluoroterphenyl-4-carboxylate (**11**) is shown in figure 2. Details of individual steps, together with the identity of intermediates (compounds **1**–**10**) and spectroscopic data obtained are given in the following section.

2.4.1. 4-Ethoxybromobenzene, 1. In a 500 ml flask equipped with condenser and magnetic stirrer, 25 g (0.1431 mol) of 4-bromophenol, 10.89 ml (0.1430 mol) bromoethane were heated under reflux overnight with 15.8 g (0.24 mol) of KOH pellets and a few crystals of KI in 300 ml of acetone [21, 22]. A yellowish oily solution with some white solids were obtained. The solids were filtered off and washed several times with ether; the washings and filtrate were recombined. This mixture was washed and extracted with water several times. The ether layer was collected and dried over $MgSO_4$. Solids were filtered off, followed by extraction with dichloromethane/water. Excess bromoethane/acetone was removed *in vacuo* and an oily liquid product was obtained. Yield>90%, 25.34 g, b.p.=233°C, ^{1}H NMR ($CDCl_3$): δ 1.45 (3H, t, $C\underline{H_3}$–CH_2–O–), 4.03 (2H, q, CH_3–$C\underline{H_2}$–O–), 6.80 (2H, d, aromatic protons *ortho* to alkoxy moiety), 7.40 (2H, d, aromatic protons *ortho* to bromine).

2.4.2. 4-Ethoxyphenylboronic acid, 2. In a 500 ml previously dry-flamed three necked flask, 25 g (0.1244 mol) of compound **1** and 150 ml dried THF were mixed and stirred thoroughly. The system was then continuously purged with N_2 and placed in a dry-ice/acetone bath, −78°C [23]. Into this flask 65 ml of 2.5 M BuLi (0.1625 mol) was added immediately but slowly through a dropping funnel. After a few minutes, 44 ml (0.1938 mol) of triisopropylborate was added, and the mixture warmed overnight to room temperature. 100 ml of 10% HCl was then added and the mixture stirred for at least 1 hour. The organic layer was extracted and the aqueous layer was washed and extracted with dichloromethane. The extracts were then combined and dried over $MgSO_4$. The filtered liquid was chromatographed through a column using hexane and ethyl acetate as eluants. Yellow solids were reprecipitated in ethyl acetate by slow addition of hexane and were recrystallized from ethanol/hexane. Solvents were removed under vacuum and white solid products collected [24]. Yield>90%, 18.57 g. ^{1}H NMR

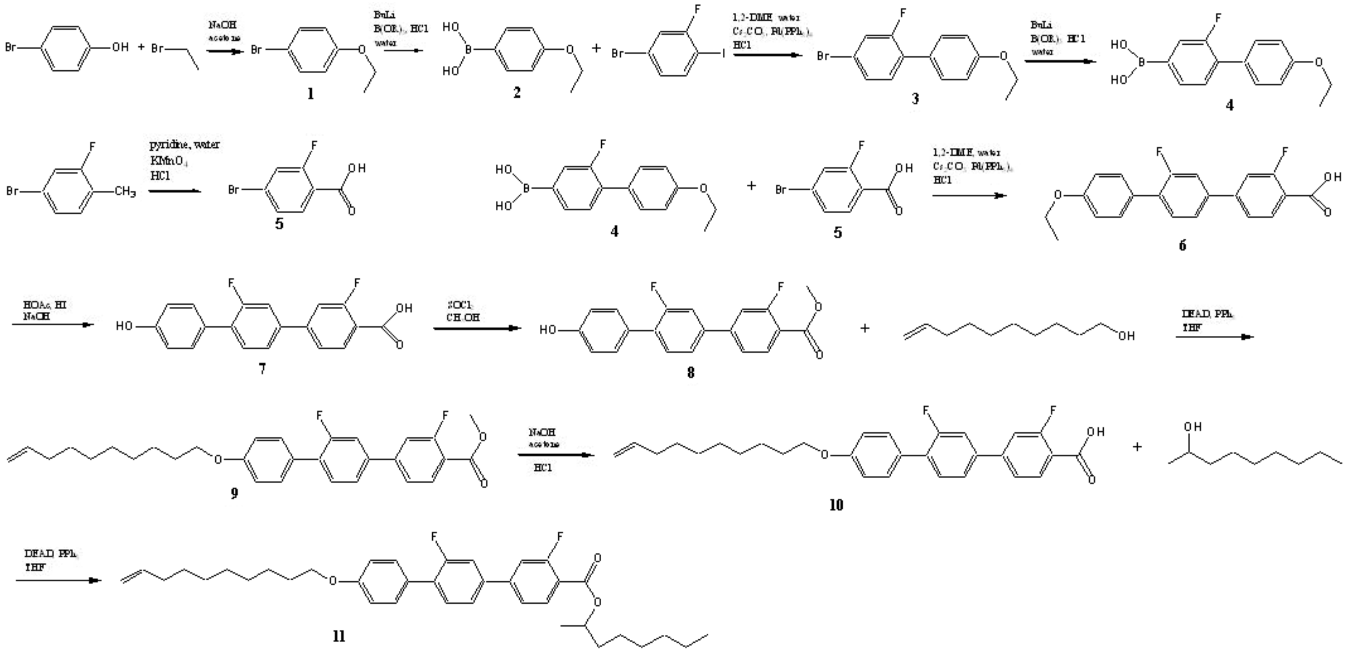

Figure 2. Synthesis of *S*-(+)-2-octyl 4″-decenyloxy-3,3′-difluoroterphenyl-4-carboxylate.

(DMSO): δ 1.35 (3H, t, $C\underline{H_3}$–CH_2–O–), 4.06 (2H, q, CH_3–$C\underline{H_2}$–O–), 6.88 (2H, d, aromatic protons *ortho* to alkoxy moiety), 7.73 (2H, d, aromatic protons *ortho* to boronic).

2.4.3. 4′-Ethoxy-3-fluorobromobiphenyl, 3. In a 1000 ml three-necked flask, 18 g (0.1085 mol) of compound **2**, 31.80 g (0.1057 mol) of 4-bromo-2-fluoro-1-iodobenzene, 41.33 g (0.1268 mol) of Cs_2CO_3, a catalytic amount of $Pd(PPh_3)_4$, 200 ml of 1,2 DME and 300 ml of water were mixed and stirred under N_2 [25–27]. This mixture was heated at reflux overnight and cooled. HCl and water were added and the product extracted twice into ether; the combined extracts were washed with brine and dried with anhydrous $MgSO_4$[28]. The solids were filtered off and some solvent removed. The solution was then treated by column chromatography, employing 1/2 hexane/CH_2Cl_2 mixture as eluant. The product was further recrystallized from hexane/ethanol; solvents were removed *in vacuo* and white solid products were obtained [22]. Yield = 85%, 26.52 g, m.p. = 65–66°C, ^{1}H NMR ($CDCl_3$): δ 1.45 (3H, t, $C\underline{H_3}$–CH_2–O–), 4.08 (2H, q, CH_3–$C\underline{H_2}$–O–), 6.97 (2H, d, aromatic protons *ortho* to alkoxy moiety), 7.31 (3H, m, inner aromatic protons), 7.44 (2H, dd, aromatic protons *ortho* to bromine).

2.4.4. 4′-Ethoxy-2-fluorobiphenyl-4-boronic acid, 4. The procedure of §2.4.2 was followed using 25 g (0.0847 mol) of compound **3**, 40 ml of 2.5M BuLi (0.1000 mol) and 27 ml (0.1189 mol) triisopropylborate as starting materials. Yield = 70%, 15.42 g, m.p. = 139–144°C, ^{1}H NMR (DMSO): δ 1.36 (3H, t, $C\underline{H_3}$–CH_2–O–), 4.09 (2H, q, CH_3–$C\underline{H_2}$–O–), 7.04 (2H, d, aromatic protons *ortho* to alkoxy moiety), 7.61 (5H, m, inner aromatic protons plus aromatic protons *ortho* to boronic acid moiety), 8.24 (1H, s, proton of –OH moiety of boronic acid functionality), IR, cm^{-1} (KBr): broad OH peak at 3346.19, strong saturated CH stretches from 2979.54 down to 2883.05 and strong aromatic CH stretches at 1593.08.

2.4.5. 4-Bromo-2-fluorobenzoic acid, $C_7H_4O_2FBr$, 5. In a 1000 ml three necked flask, 10.72 ml (0.0847 mol) of 4-bromo-2-fluorotoluene, 50 ml of pyridine and 350 ml water were mixed and stirred. 33.50 g of $KMnO_4$ (0.2115 mol) solid was added in increments while the mixture was warmed. Gentle reflux was then maintained overnight. Black MnO_2 solid was filtered off, and washed several times with hot water to wash down adsorbed products and pyridine. The filtrate and the washings were combined and reduced *in vacuo*. The mixture was cooled and acidified with 10% HCl to pH 3 or until precipitation was complete. The precipitated product was washed with a minimum of ice-cold water to remove pyridinium chloride; it was then recrystallized from acetone/hexane. Solvents were removed *in vacuo* and white solid products were collected [29]. Yield = 80%, 14.83 g, m.p. = 204–208°C. ^{1}H NMR (DMSO): δ 7.58 (1H, d, H *ortho* to Br, *para* to F and *meta* to carboxy), 7.72 (1H, d, *ortho* to Br and F, *meta* to carboxy), 7.82 (1H, dd, *ortho* to carboxy, *meta* to Br and F), IR, cm^{-1} (KBr): very broad OH peak from 2600 to 3200 and strong C(O)O peak at 1694.32.

2.4.6. 4″-Ethoxy-3,3′-difluoroterphenyl-4-carboxylic acid, $C_{21}H_{16}O_3F_2$, 6. The procedure of §2.4.3 was followed using 13.5 g (0.0519 mol) of compound **4**, 11 g (0.0502 mol) of compound **5** and 32.71 g (0.1004 mol) of Cs_2CO_3 as starting materials (solvent 50% water/50% acetone) [30]. Yield = 70%, 12.87 g, m.p. = 270–275°C. ^{1}H NMR (DMSO): δ 1.36 (3H, t, $C\underline{H_3}$–CH_2–O–), 4.09 (2H, q, CH_3–$C\underline{H_2}$–O–), 7.06 (2H, d, aromatic protons *ortho* to alkoxy moiety), 7.71 (7H, m, inner aromatic protons), 7.97 (1H, dd, aromatic proton *ortho* to carboxy moiety).

2.4.7. 4″-Hydroxy-3,3′-difluoroterphenyl-4-carboxylic acid, $C_{19}H_{12}O_3F_2$, 7. Compound **6** (10 g, 0.0282 mol) was placed in a 250 ml flask and heated at reflux overnight in a mixture of 60 ml conc. HI/15 ml conc. acetic acid. Acetone (75 ml) was used as solvent. The system was cooled, 6M NaOH added dropwise to pH 3–4, and the solid filtered off and thoroughly washed with water. It was then dissolved in ethanol and recrystallized from mixtures of ethanol/hexane [31]. Yield = 70%, 6.44 g, m.p. = >300°C. ^{1}H NMR (DMSO): δ 6.91 (2H, d, aromatic protons *ortho* to the –OH moiety), 7.46 (2H, d, inner aromatic protons), 7.67 (5H, unresolved multiplet, inner aromatic protons), 7.97 (1H, dd, aromatic proton *ortho* to the carboxy functionality), IR, cm^{-1} (KBr): broad OH peak at 3432.18 and strong C(O)(OH) peak at 1690.1.

2.4.8. Methyl 4″-hydroxy-3,3′-difluoroterphenyl-4-carboxylate, $C_{20}H_{14}O_3F_2$, 8. Compound **7** (5.0 g, 0.0153 mol) and 250 ml methanol was placed in a 500 ml flask equipped with a condenser attached to a bulb (to release gas pressure due to HCl and SO_2 production) and with a drying agent; 15.00 ml of thionyl chloride was added dropwise while gently heating the flask. A solid precipitate began to form; the system was cooled and the solvent removed *in vacuo*. The solid was collected and recrystallized from acetone/hexane mixture [32, 33]. Yield = 85%, 4.43 g, m.p. = 208–209°C. ^{1}H NMR ($CDCl_3$): δ 3.97 (3H, s, methyl protons of the ester functionality), 6.95 (2H, d, aromatic protons *ortho* to the –OH moiety), 7.49 (7H, unresolved multiplet, inner aromatic protons), 8.05 (1H, dd, aromatic proton *ortho* to the carboxy functionality).

2.4.9. Methyl 4″-decenyloxy-3,3′-difluoroterphenyl-4-carboxylate, $C_{30}H_{32}O_3F_2$, 9. A solution of 2.62 g of triphenylphosphine (PPh_3, 0.010 mol) and 1.57 g (0.010 mol) of 9-decen-1-ol in 50 ml THF was added dropwise to a solution of 1.70 ml diethylazodicarboxylate (DEAD, 0.010 mol) and 3.4 g (0.010 mol) of compound **8** in 100 ml dry CH_2Cl_2 at room temperature. The mixture was warmed, but the temperature was maintained low enough to avoid boiling. Precipitates of triphenylphosphine oxide and diethylhydrazine-dicarboxylate were immediately filtered off; the solvents were removed *in vacuo*. A white precipitate of the final product, fluorescing under UV, was obtained. Purification was by column chromatography, using high polarity hexane/acetone mixtures as eluant. Solvents were removed under vacuum and white solid products were collected [34]. Yield=57%, 2.73 g. ^{1}H NMR ($CDCl_3$): δ 1.40 (10H, m, $–O–CH_2–CH_2(C\underline{H_2})_{\underline{5}}–CH_2–CH=CH_2$); 1.85 (2H, m, $–O–CH_2–CH_2(CH_2)_5–C\underline{H_2}–CH=CH_2$); 2.08 (2H, m, $–O–CH_2–C\underline{H_2}(CH_2)_5–CH_2–CH=CH_2$); 4.05 (5H, m, $–O–C\underline{H_2}–CH_2(CH_2)_5–CH_2–CH=CH_2$ and $–CO_2–C\underline{H_3}$); 5.00 (2H, m, $–O–CH_2–CH_2(CH_2)_5–CH_2–CH=C\underline{H_2}$); 5.85 (1H, m, $–O–CH_2–CH_2(CH_2)_5–CH_2–C\underline{H}=CH_2$), 7.05 (2H, d, aromatic protons *ortho* to alkoxy moiety); 7.67(7H, unresolved multiplet, inner aromatic protons); 7.95(1H, dd, aromatic proton *ortho* to carboxy moiety), IR, cm^{-1} (KBr): weak to medium vinyl stretch at 3083.75; strong saturated CH stretches at 2933.22 and 2852.18; strong C=O(OMe) peak at 1717.48).

2.4.10. 4″-Decenyloxy-3,3′-difluoroterphenyl-4-carboxylic acid, $C_{29}H_{30}O_3F_2$, 10. The usual literature procedure was followed on the base hydrolysis of an ester, using 2 g (0.0042 mol) of compound **9** and 50 ml (0.020 mol) of 0.4M NaOH [35]. Acetone (50 ml) was used as the solvent; HCl was added to neutralize NaOH. The acetone was then removed *in vacuo*. The solids were filtered off, washed thoroughly with water, then redissolved in acetone and reprecipitated by slow addition of hexane. Purification by recrystallization from acetone/hexane gave a white solid product. Yield=88%, 1.72 g, m.p.=130–135°C. ^{1}H NMR (DMSO): δ 1.40 (10H, m, $–O–CH_2–CH_2(C\underline{H_2})_{\underline{5}}–CH_2–CH=CH_2$); 1.85 (2H, m, $–O–CH_2–CH_2(CH_2)_5–C\underline{H_2}–CH=CH_2$); 2.08 (2H, m, $–O–CH_2–C\underline{H_2}(CH_2)_5–CH_2–CH=CH_2$); 4.05 (2H, t, $–O–C\underline{H_2}–CH_2(CH_2)_5–CH_2–CH=CH_2$); 5.00 (2H, m, $–O–CH_2–CH_2(CH_2)_5–CH_2–CH=C\underline{H_2}$); 5.85 (1H, m, $–O–CH_2–CH_2(CH_2)_5–CH_2–C\underline{H}=CH_2$), 7.05 (2H, d, aromatic protons *ortho* to alkoxy moiety); 7.67(7H, unresolved multiplet, inner aromatic protons); 7.95(1H, dd, aromatic proton *ortho* to carboxy moiety), IR, cm^{-1} (KBr): broad intramolecularly H- bonded OH at 3414.13; weak to medium vinyl stretch at 3052.3; strong saturated CH stretches at 2940.4 and 2854.8; strong C=O(OH) peak at 1722.9; strong isolated or non-conjugated C=C absorption at 1624.1 and strong –OH bending at around 1260 (overlaps with assymmetric C–O–C stretch).

2.4.11. Synthesis of S-(+)-(2-Octyl) 4″-decenyloxy-3,3′-difluoroterphenyl-4-carboxylate, 11. The procedure of §2.4.9 was followed using 1.50 g (0.0032 mol) of compound **10**, 0.768 ml of *R*-(−)-2-octanol, 0.84 g of PPh_3, 0.55 ml of DEAD, 25 ml THF and 50 ml CH_2Cl_2. Yield=45%, 1.84 g; overall % yield ⩾4.5%; HPLC retention time=62.3 min, [α]20=+19, m.p.=35.5°C. ^{1}H NMR ($CDCl_3$): δ 0.90 (m, 3H, $–CO_2–CH\ CH_3–(CH_2)_5–C\underline{H_3}$); 1.60 (m, 22H, $–CO_2–CH\ CH_3–(C\underline{H_2})_{\underline{5}}–CH_3$ and $–O–CH_2–(C\underline{H_2})_{\underline{6}}–CH_2(H)–C=CH_2$); 1.82 (m, 3H, $–CO_2–CH\ C\underline{H}_3–(CH_2)_5–CH_3$); 2.08 (m, 2H, $–O–CH_2–(CH_2)_6–C\underline{H_2}(H)–C=CH_2$); 4.05 [t, 2H, $–O–C\underline{H_2}–(CH_2)_6–CH_2–C=CH_2(H)$ or Hs labelled 18 and 19); 5.00 (m or dd, 2H, $–O–CH_2–(CH_2)_6–CH_2(H)–C=C\underline{H_2}$ or Hs labelled 1 and 2); 5.23 (m, 1H, $–CO_2–C\underline{H}\ CH_3–(CH_2)_5–CH_3$ or H labelled 30); 5.85 (m, 1H, $–O–CH_2–(CH_2)_{\underline{6}}–CH_2–C=CH_2(\underline{H})$ or H labelled 3]; 7.05 (2H, d, aromatic protons *ortho* to alkoxy moiety or Hs labelled 20 and 21); 7.48 (7H, unresolved multiplet, inner aromatic protons or Hs labelled 22 to 28); 8.00 (1H, dd, aromatic proton ortho to ester moiety or H labelled 29). ^{13}C NMR ($CDCl_3$): δ 16.12 (1C, $–CO_2CH\ CH_3–(CH_2)_5\underline{C}H_3$); 22.05 (1C, $–CO_2\underline{C}H_3CH–(CH_2)_5\underline{C}H_3$); 24.66 (1C, $–CO_2CH\ CH_3–(CH_2)_4–\underline{C}H_2CH_3$); 27.72 (3C, $CH_2=CH(CH_2)_5\underline{C}H_2CH_2CH_2–O–$ and $–CO_2CH\ CH_3–CH_2\underline{C}H_2\underline{C}H_2(CH_2)_2CH_3$); 31.39 (5C, $CH_2=CH\ CH_2\underline{C}H_2\underline{C}H_2\underline{C}H_2\underline{C}H_2CH_2\underline{C}H_2–O–$); 33.85 (1C, $–CO_2CH\ CH–(CH_2)_3\underline{C}H_2CH_2CH_3$); 35.90 (1C, $CH_2=CH\underline{C}H_2(CH_2)_6\ CH_2–O–$), 38.02 (1C, $–CO_2CH\ CH_3–\underline{C}H_2(CH_2)_4CH_3$); 70.11 (1C, $CH_2=CH(CH_2)_7\underline{C}H_2–O–$); 74.43 (1C, $–CO_2CH_3\underline{C}H–(CH_2)_5CH_3$); 116.87 (5C, namely the two carbons on the first ring *ortho* to decyloxy moiety or Cs labelled 11 and 13; the third carbon is on the second ring which is *ortho* to the first F, while the fourth carbon is on the third ring *ortho* to the other F; or the Cs labelled 22 and 23 respectively; the fifth carbon is the unsaturated terminal carbon or the C labelled 1 of the alkenyloxy moiety); 120.80 (1C, the aromatic carbon *ortho* to the second F and directly attached to the –COO moiety or the C labelled 27); 124.09 (1C, the carbon on the third ring *para* to the second F or the C labelled 25); 124.69 (1C, the carbon on the second ring also *para* with respect to the first F or the C labelled 20); 128.50 (1C, the carbon on the second ring *ortho* to the F and *para* to the third ring; or the C labelled 18); 131.65 (1C, the carbon on the first ring which is *para* to the decyloxy moiety and directly attached to the second ring; or the C labelled 15); 132.10 (2C, the carbons on the first ring *ortho* to the second ring and *meta* to the decyloxy moiety or the Cs labelled 14 and 16); 132.97 (1C, the carbon on the second ring *meta* to the first F and the third ring moiety and *ortho* to the first ring or the C labelled 19); 134.62 (1C, the carbon on the third ring *ortho* to the ester moiety and *meta* to both the second ring and the second F or the C labelled 26); 141.40 (2C, the first carbon is the carbon on the second ring *meta* to the first F and directly attached to the third ring or the C labelled 21; the second carbon is the other unsaturated carbon of the alkenyloxy moiety or the C labelled 2); 147.95 (1C, the carbon on the third ring *meta* to the second F and directly attached to the second ring or the C labelled 24); 159.80 and 161.40 (1C, the carbon on the second ring directly attached to the first F or the C labelled 17; J_{C17-F}=319.2 Hz); 161.90 (1C, the carbon on the first ring directly attached to decyloxy moiety or the C labelled 12); 164.60 and 166.30 (1C, the carbon on the third ring directly attached to the second F or the C labelled 28; J_{C28-F}=339.15 Hz); 167.10 (1C, the carbon of the COO moiety or the C labelled 29), IR, cm^{-1} ($CDCl_3$): strong saturated CH stretch at 2902.35; strong C=O(O*R*) stretch at 1709.8; medium to strong C=C stretch at 1605.55).

3. Results and discussion

Compound **11** showed the phase changes K35.5SC*–47SmX–55SmA78.67I (°C) when heated from the crystalline state to the isotropic state, with the SmX range not being very visible. The $\Delta H_{\text{melting}}$ and $\Delta H_{\text{isotropization}}$ are 80.660 and 7.933 J g^{-1}, respectively. Cooling from the isotropic to the chiral smectic C phase showed the following phase changes, I75.5SmA52.50SmX47.17SmC* (°C) with the chiral smectic C phase persisting until room temperature. The cooling curve showed three small yet distinct ΔH values. The first of these is the $\Delta H_{\text{isotropization}}=-4.862$ J g^{-1}, then $\Delta H_{\text{SmA to SmX}}=-54$ mJ g^{-1} and finally $\Delta H_{\text{SmX to SmC*}}=-326$ mJ g^{-1} (see figures 3–4). Figures 5–7 show the different textures representing the different mesophases present in compound **11**.

The SmX phase is most probably a ferrielectric/antiferroelectric SmC_{α}* phase (ferroelectricity is dependent on temperature) because of the shape of the current response curve (this will be reported on in another paper) and the results of DSC [36–38]. This

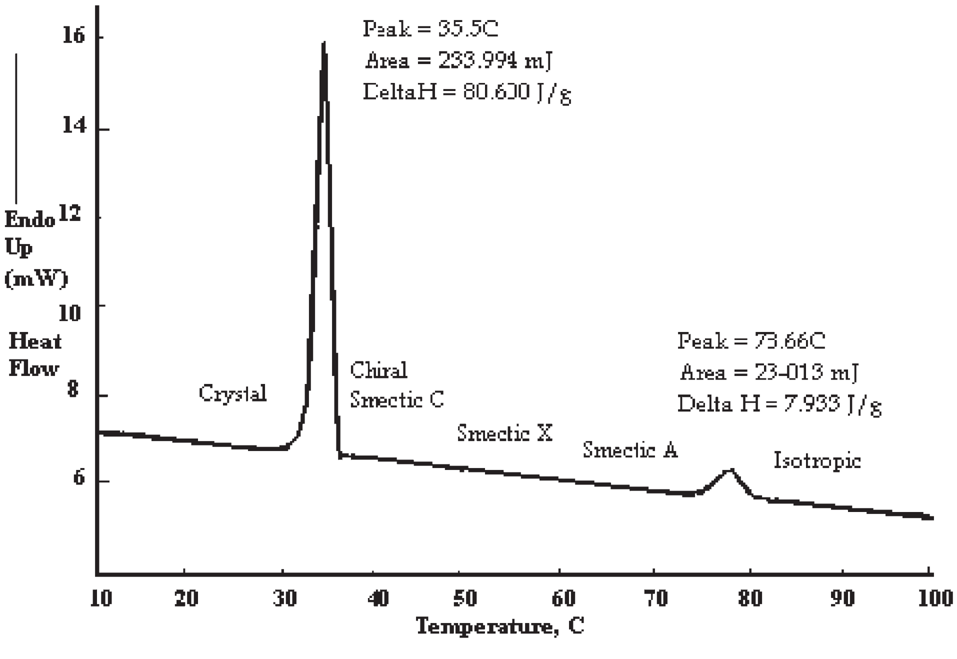

Figure 3. DSC heating curve of compound **11**.

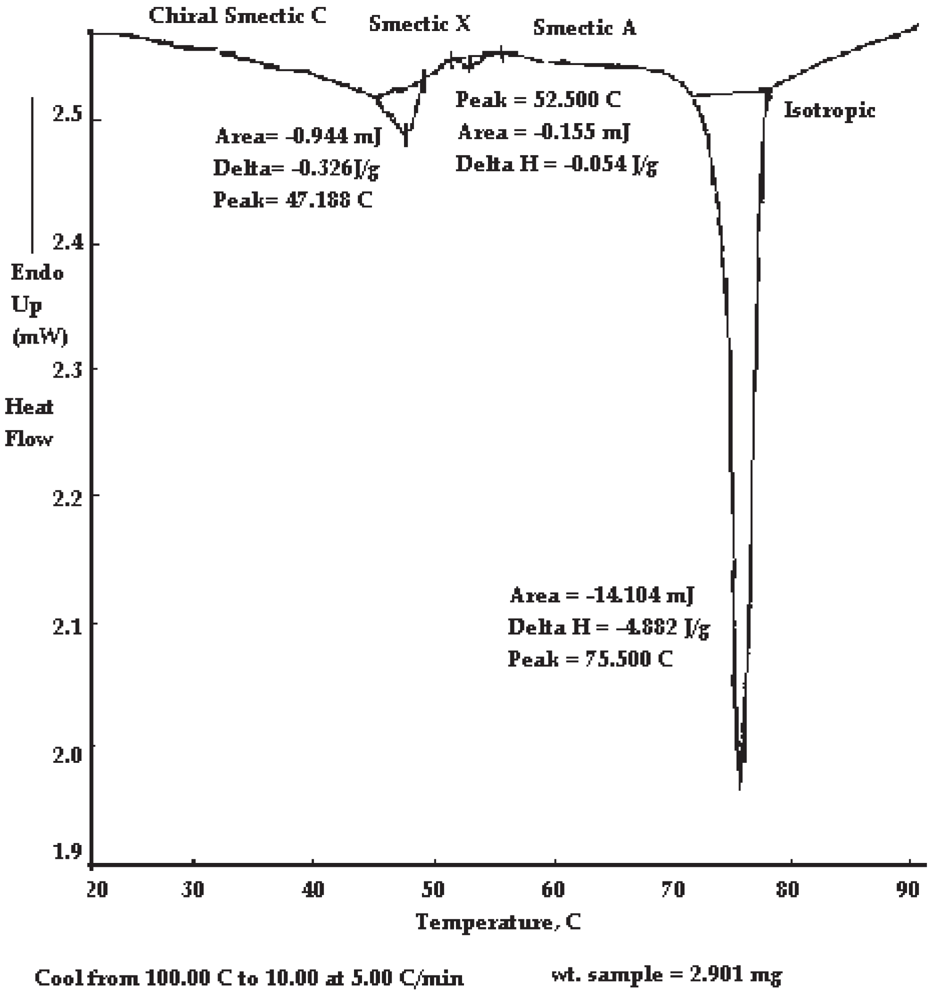

Figure 4. DSC cooling curve of compound **11**.

SmC_α* phase is very difficult to detect by optical observation because its textures are similar to those of the SmA phase [39]. The POM texture of the SmX phase is also very similar to that of the unidentified smectic phase obtained by Chen *et al.* [40]. Final confirmation of the identity of the SmX phase would entail confirmatory tests such as miscibility tests in conjunction with POM; and use of a thermal microscopy instrument configured by Carvalho *et al.* [39, 41].

Polarimetric measurement showed $[\alpha]^{20}=+19^\circ$ which is opposite to the levorotatory action of *R*-(−)octanol. This makes the final configuration around the chiral centre of compound **11** to be *S*-(+):

For *R*-(−)-2-octanol: $[\alpha]^{20}=(100)\ (-0.18^\circ)/(0.947)\ (2)=-9.5^\circ$; for IG compound: $[\alpha]^{20}=(100)\ (0.10^\circ)/(0.27)\ (2)=+18.52^\circ$.

It was also observed, as expected, that the crude acid intermediate **10** exhibited only the nematic phase as shown by the POM experiments [42] (see figures 8 and 9). The transition temperatures, specifically the clearing points, obtained in these experiments are about twice those obtained in the melting point determination on this intermediate.

4. Conclusion

This work is important in two aspects. First, it was able to produce a compound that can be used for display applications; compound **11**, is a ferroelectric liquid crystal with properties that can be configured to a surface-stabilized arrangement of molecules. Second, this study extends the use of Suzuki coupling reactions to acids (see § 2.4.3. and 2.4.6.) by using excess Cs_2CO_3 (previously done only on compounds with alkyl and alkoxy terminal chains). The electro-optical properties of the FLC will be reported in a future publication.

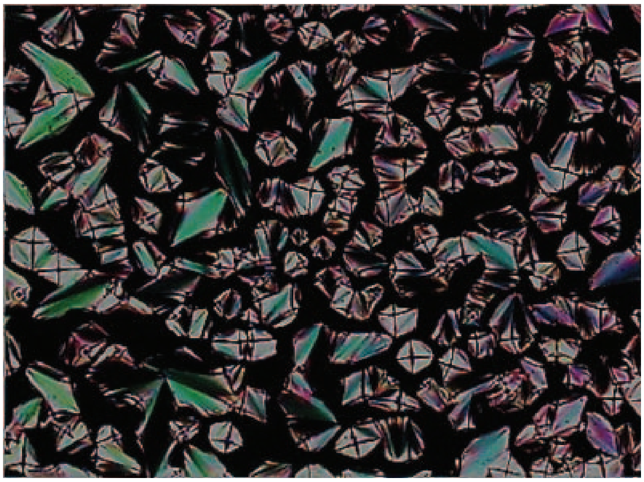

Figure 5. Smectic A crystallites of compound **11** at 78°C.

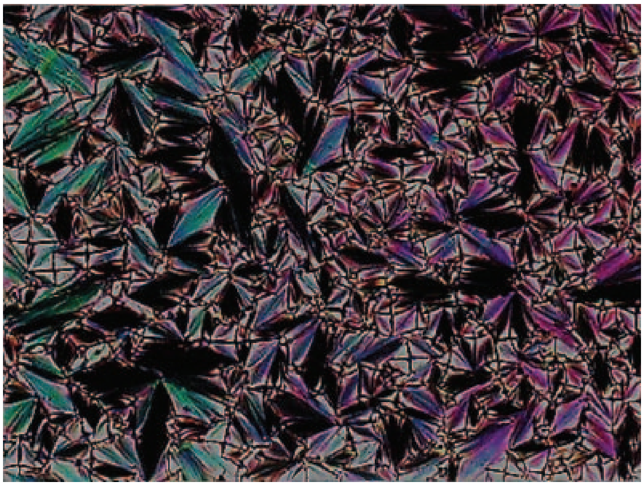

Figure 6. Smectic X (most probably a $SmC_\alpha*$) of compound **11** at 50°C. Notice the less apparent striations of the leaf-like structure.

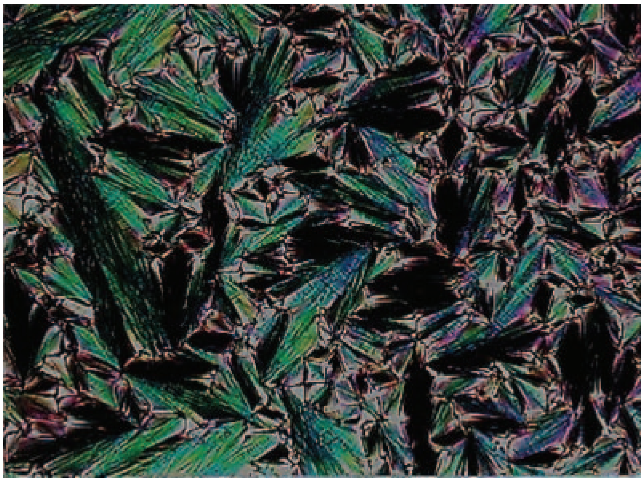

Figure 7. Smectic C crystallites of compound **11**.

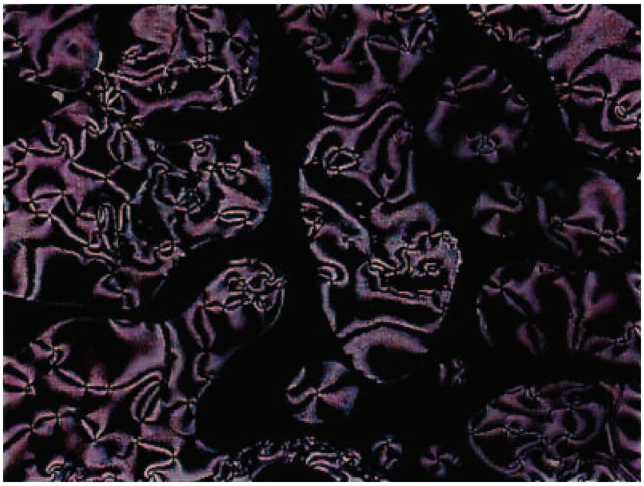

Figure 8. Nematic schlieren texture of compound **10** at 255°C.

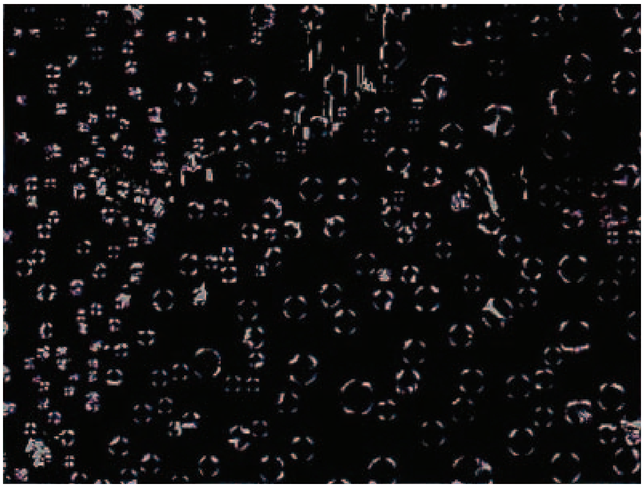

Figure 9. Nematic crystallites of compound **10** at 266°C.

Table 1. ^{1}H NMR data for compound **11**.

δ/ppm	No. of equivalent H atoms	Fragment/moiety
0.90	m, 3H	$-CO_2-CH\ CH_3-(CH_2)_5-C\underline{H_3}$
1.60	m, 22H	$-CO_2-CH\ CH_3-(C\underline{H_2})_{\underline{5}}-CH_3$ and $-O-CH_2-(C\underline{H_2})_{\underline{6}}-CH_2-(C{=}CH_2)H$
1.82	m, 3H	$-CO_2-CH\ C\underline{H}_3-(CH_2)_5-CH_3$
2.08	m, 2H	$-O-CH_2-(CH_2)_6-C\underline{H_2}-(C{=}CH_2)H$
4.05	t, 2H	$-O-C\underline{H_2}-(CH_2)_6-CH_2-(C{=}CH_2)H$
5.00	m or dd, 2H	$-O-CH_2-(CH_2)_6-(CH_2)H-C{=}C\underline{H_2}$
5.23	m, 1H	$-CO_2-C\underline{H}\ CH_3-(CH_2)_5-CH_3$
5.85	m, 1H	$-O-CH_2-(CH_2)_{\underline{6}}-CH_2-(C{=}CH_2)\underline{H}$
7.05	d, 2H	aromatic protons *ortho* to alkoxy moiety
7.48	7H, unresolved multiplet	inner aromatic protons
8.00	dd, 1H	aromatic proton *ortho* to ester moiety

Table 2. ^{13}C NMR data for compound **11**.

δ/ppm	No. of equivalent C atoms	Fragment/moiety
16.12	1C	$–CO_2CH\ CH_3–(CH_2)_5\underline{C}H_3$
22.05	1C	$–CO_2CH\ \underline{C}H_3–(CH_2)_5CH_3$
24.66	1C	$–CO_2CH\ CH_3–(CH_2)_4–\underline{C}H_2CH_3$
27.72	3C	$CH_2{=}CH(CH_2)_5\underline{C}H_2CH_2CH_2–O–$ and $–CO_2CH\ CH_3–CH_2\underline{C}H_2\underline{C}H_2(CH_2)_2CH_3$
31.39	5C	$CH_2{=}CH(CH_2\underline{C}H_2\underline{C}H_2\underline{C}H_2\underline{C}H_2CH_2\underline{C}H_2–O–)$
33.85	1C	$–CO_2CH\ CH_3–(CH_2)_3\underline{C}H_2CH_2CH_3$
35.90	1C	$CH_2{=}CH\underline{C}H_2(CH_2)_6CH_2–O–$
38.02	1C	$–CO_2CH\ CH_3–\underline{C}H_2(CH_2)_4CH_3$
70.11	1C	$CH_2{=}CH(CH_2)_7\underline{C}H_2–O–$
74.43	1C	$–CO_2\ CH_3\underline{C}H–(CH_2)_5CH_3$
116.87	5C	two carbons on the first ring *ortho* to decyloxy moiety; third carbon is on the second ring which is *ortho* to the first F; fourth carbon is on the third ring *ortho* to the other F; fifth carbon is the unsaturated terminal carbon
120.80	1C	the aromatic carbon *ortho* to the second F and directly attached to the –CO(O) moiety
124.09	1C	the carbon on the third ring *para* to the second F
124.69	1C	the carbon on the second ring also *para* with respect to the first F
128.50	1C	the carbon on the second ring *ortho* to the F and *para* to the third ring
131.65	1C	the carbon on the first ring which is *para* to the decyloxy moiety and directly attached to the second ring
132.10	2C	the carbons on the first ring *ortho* to the second ring and *meta* to the decyloxy moiety
132.97	1C	the carbon on the second ring *meta* to the first F and the third ring moiety and *ortho* to the first ring
134.62	1C	the carbon on the third ring *ortho* to the ester moiety and *meta* to both the second ring and the second F
141.40	2C	the first carbon is the carbon on the second ring *meta* to the first F and directly attached to the third ring; the second carbon is the other unsaturated carbon of the alkenyloxy moiety
147.95	1C	the carbon on the third ring *meta* to the second F and directly attached to the second ring
159.80 161.40	1C	the carbon on the second ring directly attached to the first F; $J_{C–F}=319.2$ Hz
161.90	1C	the carbon on the first ring directly attached to decyloxy moiety
164.60 166.30	1C	the carbon on the third ring directly attached to the second F; $J_{C–F}=339.15$ Hz
167.10	1C	the carbon of the CO(O) moiety

Acknowledgements

The authors wish to thank the Department of Science and Technology, the Institute of Chemistry, University of the Philippines at Diliman and the Liquid Crystal Institute, Kent State University, for their support in this research.

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