The synthesis and properties of a new series of chiral fluoro-substituted benzoxyloxybenzoates with nonchiral chains ranging from heptyloxy to octadecyloxy are reported. The mesomorphic properties of all of the compounds have been examined by a combination of optical polarized light microscopy, differential scanning calorimetry, and miscibility studies. They show rich polymorphism, and seven compounds exhibit the antiferroelectric (SmC*\textsubscript{A}) phase. The spontaneous polarization in the ferroelectric (SmC*) phase has been measured as a function of temperature for selected compounds.

Keywords: ferroelectric; antiferroelectric; liquid crystals; spontaneous polarization; miscibility

INTRODUCTION

Since the discovery of antiferroelectricity in mesogenic materials [1], a fairly large number of compounds exhibiting this phenomenon have been synthesized [2–8]. The standard material, 4-(1-methylheptyloxycarbonyl)-phenyl-4'octyloxybiphenyl-4-carboxylate [MHPOBC] has been investigated in detail as it exhibits a number of phases, and the structure of the antiferroelectric phase was established using this material [9]. Lateral substituents have been used in liquid crystal chemistry to not only modify the transition temperatures but also to alter the dipolar effects to advantage. A fluoro substituent in terms of its van der Waal’s radius is not very much different from that of hydrogen and combined with its large

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Electronegativity has been used widely to obtain useful physical properties of liquid crystalline materials. The influence of a lateral fluoro substituent in different positions of the core of many systems exhibiting antiferroelectric properties has also been examined [2,8,10]. It is known that a fluoro substituent ortho to the n-alkoxy chain in three ring triesters reduces the longitudinal dipole moment but the mesophase sequence is retained [8]. It has been reported by Demus et al. [11] that compounds with a fluoro substituent ortho to the carboxylate group containing the chiral moiety in three ring diesters show a wide temperature range of the antiferroelectric phase. The aim of the present study was to combine these two aspects, by introducing one fluoro substituent in each of the terminal phenyl rings in a three ring system and examine the mesomorphic properties with emphasis on the antiferroelectric properties. We have also compared the mesomorphic properties of this homologous series of compounds with those of the unsubstituted analogues.

**EXPERIMENTAL**

2-Fluoro-4-benzyloxybenzoic acid was prepared by first reacting ethyl 2-fluoro-4-hydroxybenzoate with benzyl chloride in the presence of anhydrous potassium carbonate in butan-2-one, followed by hydrolysis of the resulting ester with aqueous alkali. Its esterification with [S]-[+] -octan-2-ol in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-N,N-dimethylaminopyridine (DMAP) as catalyst gave compound 3. The deprotection of the phenolic group was carried out through a palladium-catalyzed hydrogenolysis reaction. The phenol 4 was condensed with the acid 5, which was prepared by treating ethyl 4-hydroxybenzoate with benzyl chloride in the presence of anhydrous potassium carbonate in butan-2-one and hydrolyzing the resulting ester with aqueous alkali, using the same esterification procedure in order to lengthen the molecule by one phenyl ring. The final compounds were obtained by a classical esterification reaction between the phenol 7 and an appropriate 3-fluoro-4-n-alkoxybenzoic acid. The 3-fluoro-4-n-alkoxybenzoic acids were prepared following a procedure described previously [12]. The purification of final compounds was carried out by column chromatography on silica gel using chloroform:petroleum ether (b.p. 60–80°C) mixture as eluent followed by repeated crystallizations using suitable solvents. The purity of all the intermediates and final compounds were checked by thin layer chromatography (Merck Kieselgel 60F_{254} precoated plates) and by normal-phase high-performance liquid chromatography using μporasil column (3.9 mm × 300 mm, Waters Associates Inc.) and 1% acetone in dichloromethane as an eluent for the latter. The chemical structures of all of
the compounds were confirmed by using a combination of $^1$H NMR spectroscopy (Bruker AMX 400 spectrometer with tetramethylsilane as an internal standard), infrared spectroscopy (Shimadzu IR 435 spectrometer) and mass spectrometry (JEOL SX 102/DA-6000). Specific optical rotations were measured using chloroform as a solvent (Optical Activity AA 1000 polarimeter).

The initial phase assignments and transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope (Leitz Laborlux 12 POL) in conjunction with a hot stage and controller (Mettler FP52 and FP5 control unit). Differential scanning calorimetry (Perkin-Elmer, Pyris 1D differential scanning calorimeter) was used to determine both the transition temperatures and the heats of transitions. The instrument was calibrated against an indium standard and all enthalpies are quoted in kJ mol$^{-1}$. Spontaneous polarization measurement was carried out using samples sandwiched between thin glass plates coated with indium tin oxide (ITO) and etched appropriately to create an active area for accurate measurement. In order to obtain sample aligned in the homogenous (planar) bookshelf geometry, the plates were treated with polyimide and rubbed unidirectionally. Mylar spacers were used to define the thickness of the cell (typically $\sim$2 to 7 μm). To perform the polarization measurements we adopted the modified form of Tower-Sawyer [13] technique proposed by Diamant et al. [14]. The measurement as a function of temperature was carried out by applying a low frequency triangular field (30–40 Hz) having an amplitude of 4–15 V$_{pp}$.

The general method of preparation of the various compounds is shown schematically in Figure 1.

The detailed procedure for the synthesis and characterization of one of the compounds under study is given below.

[S]-[+]-1-Methylheptyl 4-[4-(4-decyloxy-3-fluorobenzoyloxy)benzoyloxy]-2-fluorobenzoate(Id)

A mixture of 4-decyloxy-3-fluorobenzoic acid (0.139 g, 0.47 mmol), [S]-[+]1-methylheptyl 2-fluoro-4-(4-hydroxybenzoyloxy)benzoate (0.2 g, 0.47 mmol), 4,N,N-dimethylaminopyridine (DMAP) (0.006 g, 0.047 mmol) and dry dichloromethane (5 ml) was stirred for 5 min. To this mixture was added 4,N,N'-dicyclohexylcarbodiimide (DCC) (0.106 g, 0.47 mmol) and stirring continued overnight at room temperature. The dicyclohexyl urea formed was filtered off and the filtrate diluted with dichloromethane (20 ml). The resultant solution was washed with 5% aqueous acetic acid (3 × 30 ml), water (3 × 30 ml) and dried over Na$_2$SO$_4$. The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform:petroleum ether mixture to yield a white solid which was
FIGURE 1 Synthetic scheme for preparation of \([S]-[+]-1\text{-methylheptyl} 4\text{-[4-\((4\text{-n-alkoxy-3-flourobenzoyloxy})\text{benzoyloxy}]2\text{-fluorobenzoates.}\)
crystallized repeatedly from isopropyl alcohol (0.274 g, 80%), m.p. 101°C, [α]D25 = 20° (1 mg/ml in CHCl₃); νmax (nujol): 2950, 1730, 1720, 1710, 1610, 1460, 1280, 1240, and 1050 cm⁻¹; δ: 0.86–0.93 (6H, t, 2XCH₃), 1.27–1.9 (27H, m, 1XCH₃, 12XCH₂), 1.83–1.9 (2H, m, -CH(CH₃)–CH₂–), 4.11–4.14 (2H, t, -Ar–OCH₂–), 5.15–5.2 (1H, m, -COOCH–), 7.0–8.27 (10H, m, ArH).

RESULTS AND DISCUSSION

The transition temperatures together with the associated enthalpies for compounds of series I are summarized in Table 1. As can be seen, all the compounds are enantiotropic mesomorphic. A preliminary examination of the different mesophases was carried out as follows. Compounds Ib, Ic, Ie, and Ig exhibit all the mesophases observed in the series, and an ex-

**TABLE 1 Transition Temperatures (°C) and Enthalpies (kJ mol⁻¹) (in Italics) for [S]-[+]1-Methylheptyl 4-[4-(4-n-alkoxy-3-fluorobenzoyloxy)benzoyloxy]benzoyloxy]-2-fluorobenzoates**

<table>
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<th>SmC*₃</th>
<th>SmC*</th>
<th>SmC*₃</th>
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<td>4.62</td>
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</tr>
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</table>

†; The enthalpy could not be measured; @; total enthalpy including any other crystal-crystal transition.

Key: Cr, Crystalline phase; SmC*ₐ, Antiferroelectric phase; SmC*₃, Ferrielectric phase; SmC*, Ferroelectric phase; SmC*₂, Chiral smectic C alpha phase; SmA, Smectic A phase; I, Isotropic phase; •, Phase exists; —, Phase does not exist.
amination of compound Id under a polarizing microscope showed the following features. On cooling the isotropic liquid, focal-conic texture typical of the smectic A phase was seen (this phase could be easily aligned homeotropically to yield dark regions). On lowering the temperature, fine bands appeared on the focal-conics (banded focal-conics) which indicated the transformation to a chiral smectic C phase. On decreasing the temperature further the bands became broader and highly colored. Two other phase transitions seen in differential scanning calorimetric thermograms could not be seen clearly under these conditions.

In order to establish the identity of the mesophases, the samples were examined on different cells coated for homogeneous and homeotropic alignments and viewed under a polarizing microscope. When the isotropic liquid of compound Id was cooled in a cell treated for homogeneous alignment, uniform areas with some focal-conic defects typical of the smectic A phase [15] were seen. As the temperature was gradually decreased, this existing texture became striated with bright bands, which grew parallel to the rubbing direction. This type of texture has been observed for smectic C* phase [15]. On further cooling the sample, the striations appeared to twist, resulting in a ropelike texture. This type of texture is typically observed for SmC* phase [15]. On reducing the temperature further, stripes started growing in a direction perpendicular to the rubbing direction on the existing ropes. This texture was identical to that observed for the antiferroelectric (SmC*A) phase [15]. A typical photomicrograph of this texture is shown in Figure 2.

On cooling the isotropic liquid of compound Ib in a cell treated for a homeotropic alignment below the SmC* phase, a birefringent texture was

![FIGURE 2 Photomicrograph of compound Id showing SmC*A phase (homogeneously aligned) at 111°C.](image-url)
obtained. The characteristic feature of this phase was that the texture appeared to be in constant motion even though the temperature was held constant. This type of texture was seen for ferrielectric phase [16], and we have identified the same (SmC* y) phase for the above compound. In addition, compounds Ic, Ie, and Ig also exhibit this phase. Therefore, from these textural observations we have been able to identify that compounds discussed above exhibit SmA, SmC* x, SmC*, SmC* y, and SmC* A phases. In order to conclusively establish the identity of the different smectic phases, a miscibility study of the nonyloxy homologue (compound Ic) was carried out with the well-known standard material 4-(1-methylheptyloxy carbonyl)-phenyl-4’-octyloxybiphenyl-4-carboxylate (MHPOBC) which exhibits the above mesophases. An isobaric binary phase diagram constructed is shown in Figure 3. The mixtures were prepared as weight/weight ratio and mixed well in their isotropic states. In this diagram a complete miscibility of all the phases over the entire composition range can be seen.

A plot of the transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain is shown in Figure 4. The plot shows fairly smooth curve relationships for like transitions. These transitions could also be seen clearly in thermograms obtained on a differential scanning calorimeter.

In order to understand the effect of fluoro substituents in the present series of compounds, a comparison of the mesophases and the transition temperatures of the unsubstituted parent compounds (series II) as well as compounds of series III synthesized by Faye et al. [8] have been made. The three series of compounds are detailed below.

When a fluoro substituent is introduced ortho to the n-alkoxy chain as in series III [8], the following marginal changes are observed. The homologues with n = 9 to 12 exhibit SmC* A, SmC* F12, SmC*, and SmA phases, while homologues with n = 8 to 10 exhibit SmC* x phase in addition to the above phases. Also, none of the homologues of this series showed SmC* F12 phase. The SmC* A phase is retained as compared to the unsubstituted compounds
FIGURE 3 Miscibility phase diagram of binary mixtures of compound Ic and the standard material MHPOBC.

FIGURE 4 A plot of transition temperatures versus the number of carbon atoms in the n-alkoxy chain.
of the series II. For example, the homologue with \( n = 8 \) in series II is monotropic, but it is rendered enantiotropic with a narrow thermal range of 2°C after the introduction of the fluoro substituent. These results indicate that the steric hindrance due to the presence of the fluoro substituent is minimal, although the clearing temperatures are considerably lowered. In the case of compounds of series I where there are two fluoro substituents, one ortho to the terminal n-alkoxy chain and the other to the carboxylate group close to the chiral center, we have observed a decrease in both the melting as well as the clearing temperatures. As far as the SmC*\( \alpha \) phase is concerned, the homologues with \( n = 8 \) to 12 in all three series of compounds exhibit this phase. It is interesting to note, however, that in the present series of compounds I, this phase is not only enantiotropic but the thermal range is quite large. For example compound If has a thermal range of 50.5°C. In contrast, the parent homologues (series II) with \( n = 8 \) and 9 show metastable SmC*\( \alpha \) phase. Another significant point to note is that for sufficiently long chain lengths (compound Ih and II), the SmC*\( \alpha \) phase disappears and the SmC* phase with a wide thermal range predominates. In addition, enantiotropic SmC*\( \alpha \) phase is observed in all the homologues of this series I.

Thus, these results show that the introduction of two fluoro substituents ortho to the terminal n-alkoxy chain as well as the carboxylate group close to the chiral moiety influences the stabilization of the SmC* and SmC*\( \alpha \) phases while reducing the melting and clearing temperatures.

The temperature dependence of spontaneous polarization (\( P_S \)) was determined, and plots of \( P_S \) versus reduced temperature (\( T - T^* \)) were obtained for five homologues (compounds Id, Ie, If, Ih, and II). A typical plot obtained for compound If is shown in Figure 5.

All of the compounds of series I follow a general pattern, and \( P_S \) was found to decrease with increase in temperature. The value lies close to zero at \( T^* \) (\( T^* \) is the SmC*\( \alpha \)-SmC* transition temperature). One of the interesting features is that a decrease in the magnitude of the polarization values was observed with an increase in the chain length. A plot of \( P_S \) at \( T - T^* = -4^\circ C \) as a function of chain length is shown in Figure 6. It can be seen that for \( n = 10 \), the value for \( P_S \) is about 61 nC/cm\(^2\), whereas for \( n = 18 \), it is reduced to about 51.5 nC/cm\(^2\).

The effect of a polar substituent on the magnitude of \( P_S \) can be explained in terms of (1) proximity between the lateral polar group and the chiral center and (2) the favorable orientation of the dipoles of the polar group and the chiral moiety. It is believed that a polar group present close to the chiral center increases \( P_S \) due to the restricted internal rotation of the polar group by steric hindrance with the chiral group [17]. This is true in systems having ether as the linking group between the chiral moiety and the core. However, when the linking group is a carboxylate group, the increase or decrease in the magnitude of \( P_S \) due to the presence of a lateral
FIGURE 5 Plot of spontaneous polarization versus reduced temperature for compound If.

FIGURE 6 Plot of the spontaneous polarization at $T-T^* = -4^\circ C$ as a function of the $n$-alkoxy chain length.
polar substituent depends on the direction of orientation of the dipoles associated with the polar group and the chiral group. This is because in the latter case, since the chiral tail is conformationally correlated with the core less tightly than in the former case, the internal rotation of the polar group becomes more feasible and hence the dipoles can orient appropriately. An increase in the value of $P_S$ is observed when the dipoles add up and a decrease in the value is seen when they cancel each other. The favorable orientation of the dipoles thereby either opposing each other or adding to each other in turn depend on the stable conformation the molecule would prefer to take so as to relieve the dipole-dipole interaction between the polar substituent and the group linking the core to the chiral moiety.

The results obtained from the measurement of spontaneous polarization for the decyloxy homologue of the difluoro (series I), parent (series II), and monofluoro (series III) substituted compounds are given below:

<table>
<thead>
<tr>
<th>Series</th>
<th>$P_S$ (nC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series I</td>
<td>$64$</td>
</tr>
<tr>
<td>Series II</td>
<td>$80$</td>
</tr>
<tr>
<td>Series III</td>
<td>$100$</td>
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</table>

It is seen that for compound that has a fluoro substituent ortho to the $n$-alkoxy chain (serie III) the value of $P_S$ is about 100 nC/cm$^2$, which is higher as compared to the unsubstituted parent compound (series II). However, when a second fluoro substituent is introduced close to the chiral center (series I), the value of $P_S$ decreases to about 64 nC/cm$^2$. This decrease in the value of spontaneous polarization may be explained as follows. The 1-methylheptyl group is slightly away from the core and is separated from it by a carboxylate group. The fluoro substituent, which is ortho to this carbonyl group, is free to orient itself so as to relieve the dipole-ortho interaction with the carbonyl group and adopt a conformation as shown below.

![Chemical Structure](image)

It is probable that in this stable conformation the dipole of the lateral fluoro substituent is opposing that of the carbonyl group, as a result of which there is a decrease in the value of $P_S$. 

Benzoyloxybenzoates Exhibiting an $SmC_a$ Phase
To summarize, a new homologous series of difluoro-substituted compounds have been synthesized. The fluoro substituents, while reducing the melting and clearing temperatures, have enhanced the thermal range of the SmC* and SmC* A phases when compared with those of the unsubstituted parent compounds. In addition, it has been found that the value of spontaneous polarization decreases as a result of introduction of outer edge fluoro substituent close to the chiral moiety.

REFERENCES