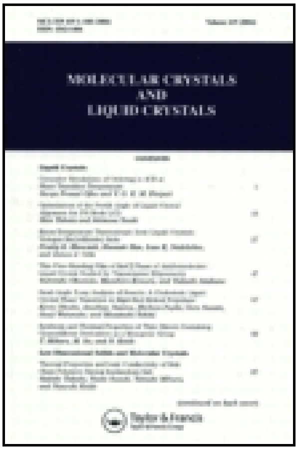

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The Liquid-Crystalline Properties of Some Chiral Derivatives of the 4-n-Alkanoyloxbiphenyl-4′-Carboxylic Acids

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THE LIQUID-CRYSTALLINE PROPERTIES OF SOME CHIRAL DERIVATIVES OF THE 4-n-ALKANOYLOXBIPHENYL-4-'-CARBOXYLIC ACIDS

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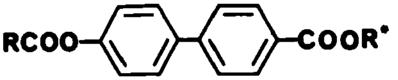
Abstract A variety of chiral derivatives of some 4-n-alkanoyloxybiphenyl-4′-carboxylic acids were prepared in order to produce a number of structurally related homologous series of compounds. In this systematic study, the synthesis of a number of chiral 2-chloropropyl, 3-chlorobutyl, alkylether, and 1-methylalkyl esters of these acids are reported. The liquid-crystalline and ferroelectric properties of these materials were also investigated and the results obtained are compared with those previously established for the closely related 1-methylpropyl, 2-methylbutyl, and 3,7-dimethyloctyl esters of the same acids.

INTRODUCTION

Interest in ferroelectric liquid-crystalline materials has increased recently because of their potential applicability to a wide variety of devices such as displays,[1] light-shutters,[2] pyroelectric detectors[3] and spatial light-modulators.[4] Consequently, an understanding of the relationship between molecular structure and the ferroelectric liquid-crystalline properties of these materials is desirable in order to exploit their potential for such applications.

Smectic liquid crystals possessing ferroelectric mesophases, high spontaneous polarizations, (Ps), low viscosities, and mesogenic phases that exist over wide temperature ranges including room temperature are required for preparing mixtures for use in device applications. Hence, the synthesis of new materials and the investigation of their properties are of central importance to the development of these device media.

In our previous studies, the ferroelectric and liquid-crystalline properties of three closely related homologous series,



R= C_7 - C_{13}

R*= (I), (II), (III)

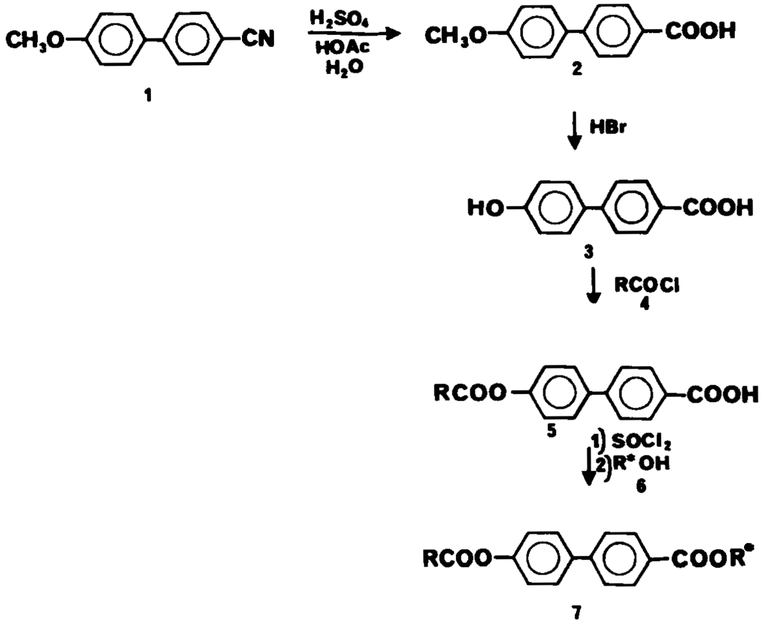
(I) R-1-methylpropyl, (II) S-2-methylbutyl, and (III) S-3,7-dimethyloctyl 4-n-alkanoyloxybiphenyl-4'-carboxylates were examined.[5] These series were selected as candidates for study in order to investigate how liquid-crystalline properties are effected by the position of the chiral center as it is moved sequentially away from the biphenyl core along the terminal aliphatic chain. For example, in series I the chiral center is adjacent to the core, whereas in series III it is removed by two carbon atoms along the spacer chain. These materials were found to exhibit a variety of smectic phases including the ferroelectric C* and crystal (J*) modifications. Several members of these series also exhibited liquid-crystalline phases that existed over reasonable temperature ranges, i.e. 10-33°, including room temperature, thus, making them potentially useful candidates for mixture purposes.

In the course of studying the effect of temperature on the magnitude of the spontaneous polarization for these series, it was found for series II that the sign of the spontaneous polarization inverts with respect to temperature.[5,6,7] For example, it was observed that at the A to C* phase transition the polarization rapidly increased. On cooling it reached a maximum value before falling and vanishing at a characteristic temperature. On further cooling the polarization reappeared, but with the opposite sign. At high temperatures the sign of the polarization was found to be negative, but at lower temperatures it was determined to be positive.

In the present investigation, we prepared a variety of biphenyl esters in order to make some comparisons of materials where the chiral end groups were varied relative to the same biphenyl core structure used in the previous study. Thus, four homologous series of compounds were synthesized in which the chiral end group was altered to produce esters of the following type; chiral ether, 2 and 3-chloroalkyl, and 1-methylalkyl ester derivatives of the 4-n-alkanoyloxybiphenyl-4′-carboxylic acids. The ferroelectric, liquid-crystalline properties, and syntheses of these series are discussed in the following sections.

EXPERIMENTAL

The 4-n-alkanoyloxybiphenyl-4′-carboxylic acids (5), scheme I, were prepared from 4-methoxy-4′-cyanobiphenyl (1) (M3, BDH chemicals) by

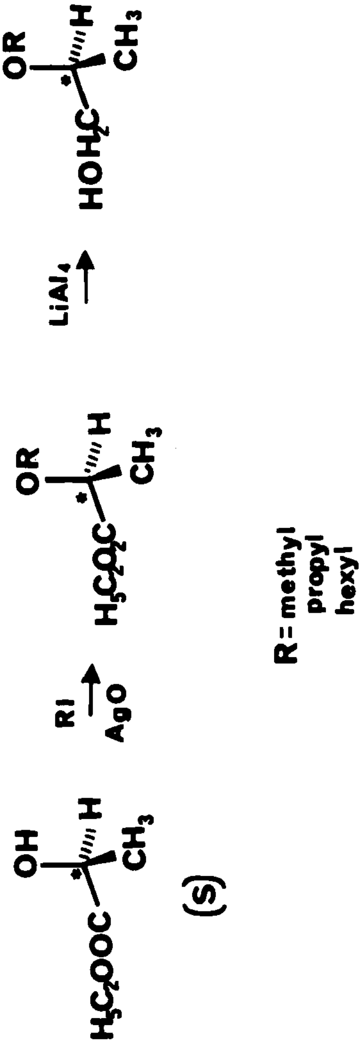

CH$_3$O
CN
1
H$_2$SO$_4$
HOAc
H$_2$O
CH$_3$O
COOH
2
HBr
HO
COOH
3
RCOCl
4
RCOO
COOH
5
1) SOCl$_2$
2) R* OH
6
RCOO
COOR*
7

Scheme I

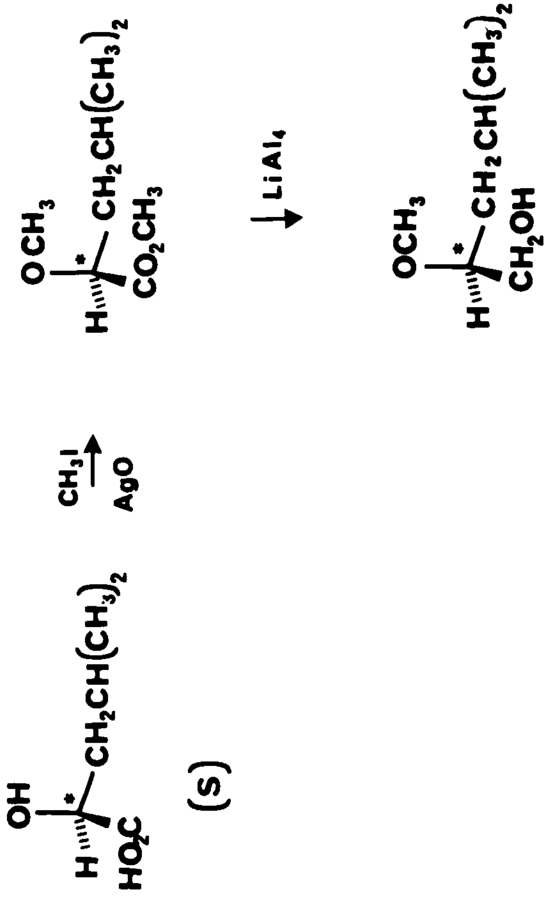
standard methods reported previously.[8] Initially, the cyano group was hydrolyzed by a mixture of concentrated sulfuric acid, water and glacial acetic acid to give the resulting 4-methoxybiphenyl-4'-carboxylic acid (2). This acid was then demethylated in the presence of hydrobromic acid (48% wt/vol in water) in glacial acetic acid to give the difunctional compound, 4-hydroxybiphenyl-4'-carboxylic acid (3). The hydroxyl group of this acid was then esterified with the appropriate n-alkanoyl chloride in the presence of pyridine, toluene and tetrahydrofuran (THF). Condensation of the acid function (5) with an optically active alcohol, the preparations of which are described below, gave the desired 4-n-alkanoyloxybiphenyl-4'-carboxylates (7).

The optically active chiral ether-alcoholic substrates were prepared by alkylating the hydroxyl group of L-ethyl lactate (Aldrich), or L-hydroxy isocaproic acid (Aldrich) with an excess of the appropriate n-alkyl iodide in the presence of silver (II) oxide[9] as outlined in Schemes 2 and 3, respectively. The resulting esters were reduced to give the desired chiral alcohols. The various chiral alcohols that were prepared by this method, along with their yields and boiling points are listed in Table 1.

The 2-chloropropyl alcoholic substrate was prepared *via* the reduction of (R)-(+)-methyl 2-chloropropionate (Aldrich).[10] The 3-chlorobutyl alcohol was prepared by initially chlorinating (R)-(−)methyl 3-hydroxybutyrate with phosphorus pentachloride followed by reduction to the


H5C2OOC
OH
H
CH3
(S)
RI
AgO
H5C2O2C
OR
H
CH3
LiAl4
HOH2C
OR
H
CH3
R = methyl
propyl
hexyl

Scheme 2


OH
H
HO_2C
$CH_2CH(CH_3)_2$
(S)
CH_3I
AgO
OCH_3
CO_2CH_3
$CH_2CH(CH_3)_2$
$LiAl_4$
OCH_3
$CH_2CH(CH_3)_2$
CH_2OH

Scheme 3

alcohol.

The optically active secondary alcohols were obtained commercially (Aldrich and Chemical Dynamics) and were used without further purification in the final esterification step to give the 1-methylalkyl derivatives.

The final products were purified by column chromatography over silica-gel (60-200 mesh) using methylene chloride and hexane (1:1) as the eluant. The products were then recrystallized from petroleum ether (bp. 35-65°C) or acetonitrile until they had attained constant transition temperatures.

The structural assignment of each synthesized compound was determined by NMR (^{1}H) and IR spectroscopy. The relative purities of the materials were determined by high pressure, reverse phase, liquid chromatography over octadecylsiloxane (5 μm, 25 cm × 0.46 mm). Acetonitrile was used as the eluant and UV spectrometry (254 nm) was employed to detect the eluting fractions.

The transition temperatures and phase classifications were determined by optical microscopy using a Zeiss universal polarizing light microscope in conjunction with a Mettler FP52 microfurnace and FP5 control unit. Differential scanning calorimetry, using a Perkin-Elmer DSC-4-TADS system was employed to measure the enthalpies of the phase transitions and to confirm the transition temperatures that were obtained by optical microscopy.

The magnitude of the spontaneous polarization was determined by the triangular wave method as a function of temperature.[11,12]

RESULTS

The alkylated chiral hydroxyether substrates prepared; 1-hydroxy-2-methylethylmethyl ether, 1-hydroxy-2-methylethylpropyl ether, and 1-hydroxy-2-methylethylhexyl ether were used to synthesize series A, B, and C respectively. The transition temperatures and phase types for these carboxylates are shown in Tables 2-4, inclusive.

Each ester in the three homologous series was shown by optical microscopy to exhibit a smectic A phase. In series A, the smectic A phase has a large temperature range for the n-nonanoyloxy and the n-undecanoyloxycarboxylates. Within this series, only the n-octanoyloxy member possesses a monotropic smectic A phase. When the transition temperatures were plotted as a function of increasing alkyl chain length, series A, B and C were found to exhibit the expected alternation trends in transition temperature for the odd and even members of the series. The 1-hydroxy-2-methylethylpropyl ether carboxylates (series B) were shown to possess smectic A and smectic I* phases for the n-octanoyloxy to n-decanoyloxy esters inclusive. The n-undecanoyloxy homologue, however, does not appear to possess the smectic I* phase. As the chain is increased

TABLE 1

Chiral Alcohols for Ether Derivatives	bp, °C	Yield %
$CH_3O\overset{*}{C}H(CH_3)CH_2OH$	120-130	49
$C_3H_7O\overset{*}{C}H(CH_3)CH_2OH$	155	66
$C_6H_7O\overset{*}{C}H(CH_3)CH_2OH$	190-200	80
$(CH_3)_2CHCH_2\overset{*}{C}H(OCH_3)CH_2OH$	175	73

TABLE 2

Series A

Transition temperatures (°C) for the homologous series

$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2\overset{*}{C}H(CH_3)OCH_3$

n	Crys.		A		Iso	Recrys.
8	•	49.6	(•	48.3)	•	18
9	•	35.8	•	52.6	•	30.1
10	•	53.0	•	54.4	•	32.4
11	•	47.0	•	58.0	•	42.9

( ) — monotropic phase transition

TABLE 3

Series B

Transition temperatures (°C) for the homologous series

$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2\overset{*}{C}H(CH_3)OC_3H_7$

n	Crys.		I*		A		Iso	Recrys.
8	•	28.0	(•	21.1)	•	44.2	•	<15
9	•	33.1	(•	28.0)	•	50.0	•	25
10	•	39.8	(•	32.1)	•	49.6	•	29.8
11	•	—	—	47.0	•	58.0	•	43.3
13	•	58.2	—	—	—	60.4	•	53.4

( ) — monotropic phase transition

TABLE 4

Series C

Transition temperatures (°C) for the homologous series

$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2\overset{*}{C}H(CH_3)OC_6H_{13}$

n	Crys.		A		Iso	Recrys.
8	•	RT	•	39.7	•	<16
9	•	35.7	•	44.4	•	23.5
10	•	38.9	•	46.3	•	26.9
11	•	47.1	•	48.4	•	39.7

RT — melts at approximately room temperature to the n-tridecanoyloxy homologue, all liquid-crystalline properties disappear because the recrystallization temperature increases so as to negate liquid crystal phase formation. Finally, it is interesting to note that the n-octanoyloxy member of series C is in the smectic A phase at room temperature and has a recrystallization temperature that is lower than 16°C. It is also interesting that none of these materials were found to exhibit the desired C* phase.

The chiral ether substrate, 3-methyl-2-methoxypentanol was used in the synthesis of the last set of ether carboxylate compounds, series D. The transition temperatures for the compounds prepared are listed in Table 5. These materials were also found to exhibit smectic A phases and no smectic C* phases. However, the ferroelectric properties of these materials were investigated in mixtures utilizing 4-n-octyloxyphenyl 4-n-decyloxybenzoate, as the achiral host. It was found from these investigations that the inversion of the spontaneous polarization sign observed in the previous study[5] was also present for mixtures of the methoxy isocaprolates with the achiral host as shown in Fig. 1. In this figure, the modulation amplitude is shown as a function of temperature for one particular mixture. At the point where its value vanishes, the sign of the spontaneous polarization inverts and the magnitude of the polarization passes through zero.

Overall, the four chiral ether carboxylate series were found to have low temperature mesogenic phases, e.g. 21-53°C. One noticeable difference

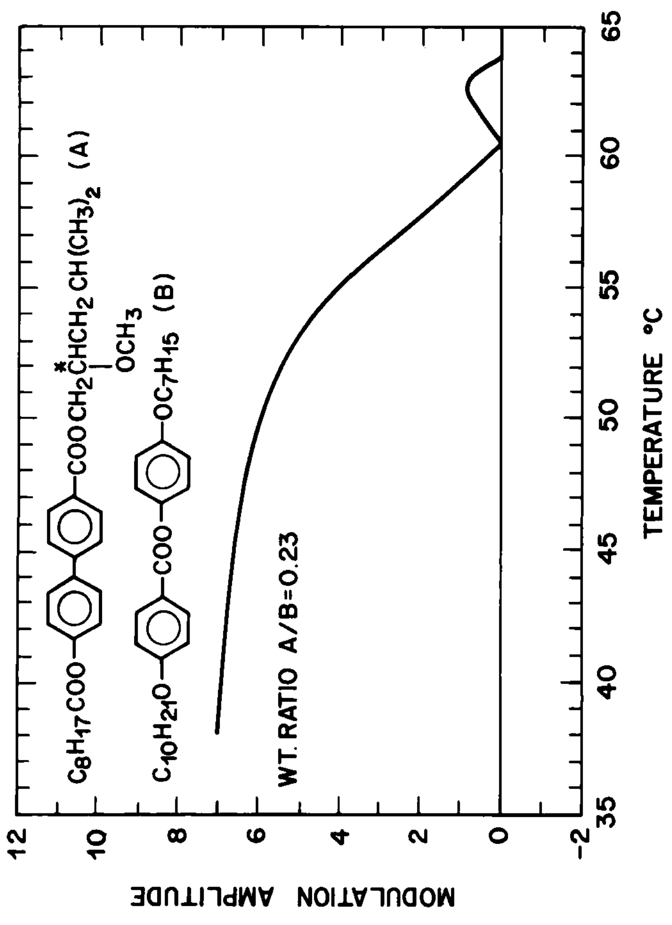


Fig. 1 The modulation amplitude of the electro-optic effect shown as a function of temperature for a mixture of 2-methoxy-5-methylpentyl, 4-n-octanoyloxybiphenyl-4'-carboxylate (A) and 4-n-heptyloxyphenyl 4-n-decyloxybenzoate (B) wt ratio A/B = 0.23.

in the comparative study between the ether carboxylates and the previously investigated series (I), (II), and (III) is that the former compounds lack a smectic C* phase. Recently some benzoate equivalents[13] were found to show smectic C* phases, however, their temperature ranges are also reduced in comparison to their alkyl analogues. This indicates that these particular chiral end groups have a poor affinity for the smectic C* phase.

The 2-chloropropyl carboxylates, series E, shown in Table 6 have similar phase properties to the compounds described above, in that they exhibit A phases but no smectic C* phases. The members within this series differ markedly when the alkanoyl chain length is increased. For example, the n-octanoyloxy homologue possesses crystal E, hexatic B and smectic A phases, whereas the n-nonanoyloxy member has only a smectic A phase.

The transition temperatures and phase types that were obtained for the analogous 3-chlorobutyl carboxylates, series F, are listed in Table 7. This series contains one extra carbon atom between the chiral center and the core in comparison to the 2-chloropropyl carboxylates (series E). This results in a completely different phase morphology for the homologous series. Each member of this homologous series was found to exhibit smectic A and J* phases with the exception of the n-octanoyloxy homologue, which was found to possess an additional smectic I* phase. The last member investigated, the n-tridecanoyloxy homologue loses the crystal J* phase and shows only the smectic A phase. This series also exhibits a

TABLE 5

Series D

Transition temperatures (°C) for the homologous series

$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2\overset{*}{C}H(OCH_3)CH_2CH(CH_3)_2$

n	Crys.		A		Iso	Recrys.
8	•	31.7	•	31.7	•	24.4
9	•	38.2	(•	37.2)	•	33.3
10	•	41.5	•	43.4	•	34.5
12	•	51.7	[•	39.8]	•	42.3

( ) — monotropic phase transition
[ ] — virtual phase transition

TABLE 6

Series E

Transition temperatures (°C) for the homologous series

$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2\overset{*}{C}H(Cl)CH_3$

n	Crys.		E		B		A		Iso	Recrys.
8	•	61.3	(•	30.5)	•	69.7	•	90.2	•	—
9	•	—	—	—	—	48.4	•	80	•	34.8

( ) — monotropic phase transition

TABLE 7

Series F

Transition temperatures (°C) for the homologous series

$$C_nH_{2n+1}COOC_6H_4C_6H_4COOCH_2CH_2\overset{*}{C}H(Cl)CH_3$$

n	Crys.		J*		I*		A		Iso	Recrys.
8	•	50.4	•	53.2	•	53.2	•	65	•	35.5
9	•	53.8	•	—	—	57.4	•	67.5	•	32.5
10	•	58.4	•	—	—	60.3	•	68.2	•	—
11	•	66.2	(•	63.7)	—	—	•	69.3	•	49.5
13	•	70.6	—	—	—	—	(•	69.6)	•	63.2

( ) — monotropic phase transition

TABLE 8

Series G

Transition temperatures (°C) for the homologous series

$$C_8H_{17}COOC_6H_4C_6H_4COO\overset{*}{C}H(CH_3)(CH_2)_nCH_3$$

n	Crys.		C*		A		Iso
1	•	50.2	(•	26.4)	•	(45.6)	•
2	•	46.2	—	—	•	(38.4)	•
3	•	29.6	—	—	•	32.6	•
4	•	37.0	—	—	•	(31.9)	•
5	•	34.3	—	—	•	(26.3)	•

( ) — monotropic phase transition

pronounced alternation effect for the odd and even members. The mesogenic phases are also present at relatively low temperatures, 53-63°C. Comparison of the two chloro homologous series with series (I), (II), and (III), appears to show that replacement of the methyl group with a chloro atom favors formation of the crystal J* mesogenic phase in place of the smectic C* phase. The spontaneous polarizations were found to be larger for the 3-chloro compounds, ~20-25 nC cm^{-2} compared to ~3-9 nC cm^{-2} for the related methyl compounds. The differences in the effect of temperature on the spontaneous polarization are shown in Figs. 2 and 3 for the two compounds, S-3-chlorobutyl 4-n-octanoyloxybiphenyl-4'-carboxylate and S-3,7-dimethyloctyl 4-n-decanoyloxybiphenyl-4'-carboxylate respectively. Interestingly, the temperature dependence of the spontaneous polarization of the chloro compounds follow the expected course, i.e. a power law type of dependency,[1] however, this is not necessarily the case for the methyl compounds.

The transition temperatures for the 1-methylalkyl carboxylates, series G, are listed in Table 8. In this series, only the 1-methylpropyl member exhibits a smectic C* phase transition. This value is in fact very close to room temperature, (26.4°C, see Fig. 4). However, the A to C* phase transition temperatures drop dramatically for the later members. From extrapolations obtained from miscibility studies, these materials were found to have virtual A to C* phase transitions well below 0°C. For example, the

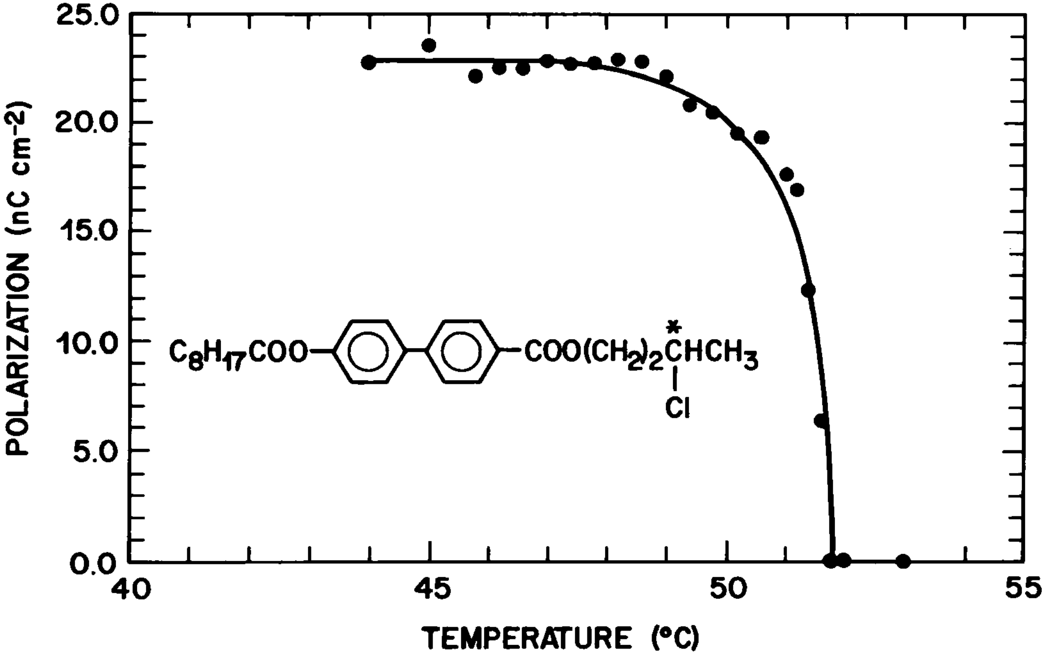


Fig. 2 The spontaneous polarization (nC cm^{-2}) shown as a function of temperature for S-3-chlorobutyl 4-n-octanoyloxybiphenyl-4′-carboxylate.

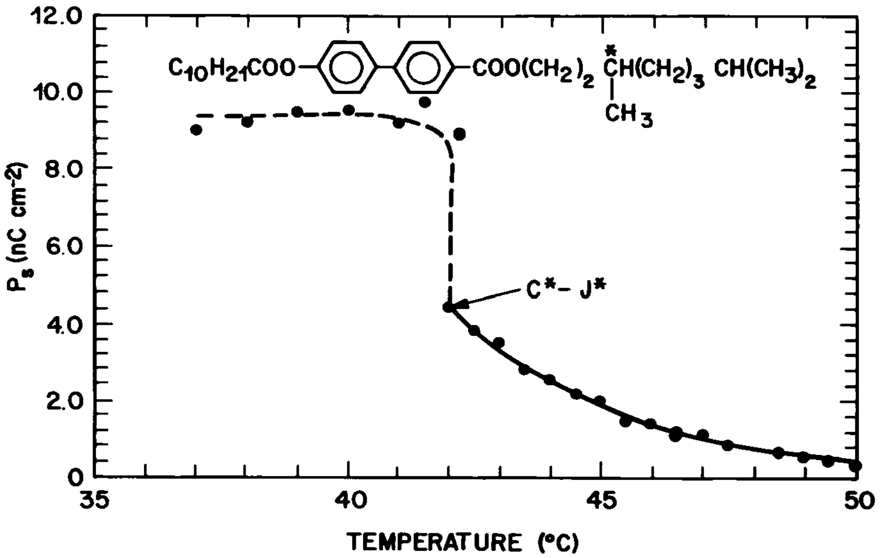


Fig. 3 The spontaneous polarization (nC cm^{-2}) shown as a function of temperature for 3,7-dimethyloctyl 4-n-decanoyloxybiphenyl-4′-carboxylate.

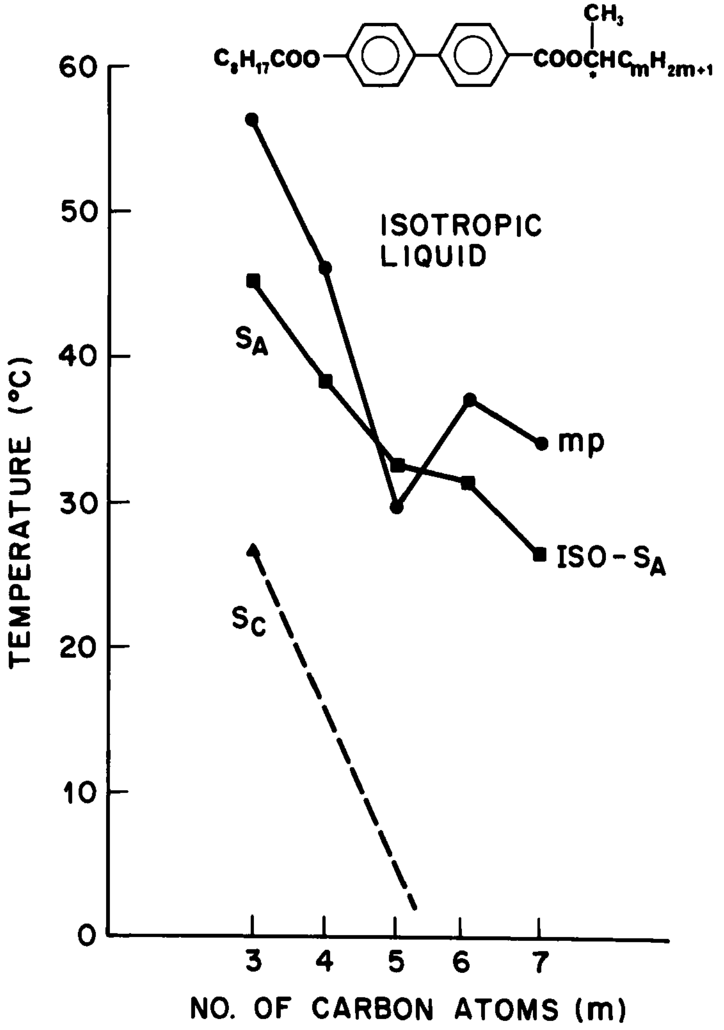


Fig. 4 The transition temperature plotted as a function of increasing alkyl chain length for the 1-methylalkyl 4-n-octanoyloxybiphenyl-4'-carboxylates.

virtual A to C* transition for the (R) or (S)-1-methylheptyl homologue was found to be below −30°C. Hence, it appears that increasing the chain on the external side of the chiral center also strongly disfavors the C* phase. This may be attributed to rotational damping of the chiral center which leads to an increase in the repulsive steric interactions between neighboring molecules, thus depressing phase formation.

DISCUSSION

The structure of the smectic C* phase is such that the constituent molecules are arranged in diffuse layers and are tilted with respect to the layer planes. The molecules within the layers are locally hexagonally close-packed with respect to the director of the phase. This ordering is only short range, extending over distances of ~15Å.[14] Generally, the intermolecular separation is between 4 and 5Å for molecules in the smectic C* phase. Consequently, disturbance of the close molecular packing arrangement may strongly effect the stability of the smectic C* phase. Disturbance in the layers can be produced by either dipolar or steric forces.

In the ether compounds, the dipolar effect is increased in the region of the chiral center because of the presence of an oxygen atom adjacent to the asymmetric carbon atom. However, the aliphatic spacer chain between the aromatic core and the ether oxygen is of a sufficient length so as to prevent conjugation of the ether oxygen with the delocalized electrons of the core.

This will essentially produce stronger hard core repulsions between neighboring molecules in a three body packing system because the oxygen atom is relatively unpolarizable in this position. Consequently, repulsive effects may be responsible for disturbing the molecular packing, thus depressing the formation of the C* phase.

Similarly, this effect is also involved in the intermolecular interactions for the 2-methoxy isocaproic carboxylates. Again there are strong hard core repulsions because of the lack of polarizability due to there being no conjugation between the ether oxygen and the aromatic core. In addition to the dipolar effect, there is also a stronger steric repulsion caused by the methoxy lateral branch. The methoxy branch this time is forced into a more off-axis location with respect to the branched 4-methylpentyl chain which will probably tend to lie along the long axis. This results in stronger steric repulsions than for a methyl branched system.

In the study of the behavior of the spontaneous polarization of one of the 2-methoxy isocaproic homologues, it was necessary to blend it with 4-n-heptyloxyphenyl 4-n-decyloxybenzoate in order to obtain a chiral smectic C* phase. As described previously, certain binary mixtures were found to exhibit inversion properties of the spontaneous polarization. This inversion was found to be concentration dependent[15] (see Fig. 1). The inversion phenomena has already been observed in pure materials such as S-2-methylbutyl 4-n-decanoyloxybiphenyl-4'-carboxylates, series (II). The change in the sign of the spontaneous polarization, in this case, was suggested to be related to various competing species of different molecular conformations that were expected to be present in the mesophase.[5,7] Similarly, possible interconverting conformations for the 2-methoxy isocaproic carboxylate may be responsible for the inversion of the spontaneous polarization (see Fig. 5). In this figure the two conformational species have opposed dipole directions at their chiral centers, hence they will have opposite spontaneous polarization directions. However, in mixtures with an achiral host the concentrations of these two species will vary both with temperature and concentration of the host.[15] Consequently, inversions in the direction of the polarization are possible, depending on these two factors.

The lack of the smectic C* phase in the chloro compounds can be directly related to the increased off-axis dipolar effect of the chloro atom at the chiral center. This interaction which appears to depress the C* phase, seems instead to favor the formation of the G or E phases. Comparison of Figs. 2 and 3, shows that the magnitude of the spontaneous polarization for the chloro compound is at least two times larger than that for a related methyl compound even though the methyl homologue has a longer external chain. Thus the increase in the spontaneous polarization is expected to be directly related to the increased dipole at the chiral center and also to the damping of the molecular rotation due to the more ordered structure of the

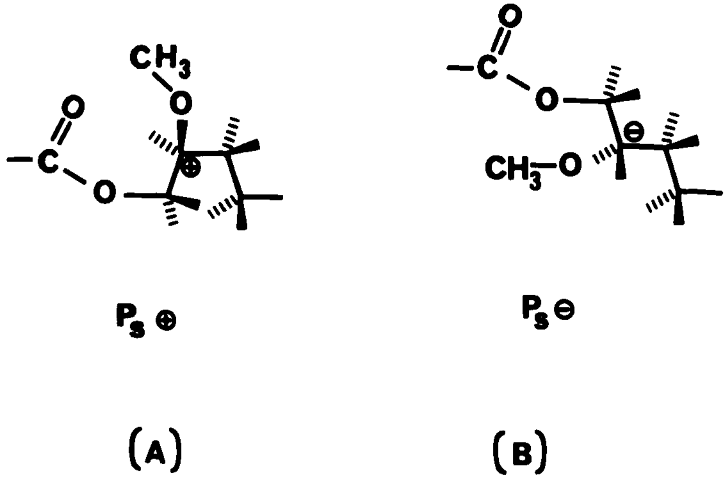


Fig. 5 Different interactions of the lateral methyl branch of the chiral center produced by bond rotation.

G phase.

The 1-methylalkyl series[16] was used to study how the spontaneous polarization of a series of compounds is effected by progressively damping of the motion of the chiral center. This particular series was selected for the study because the effect on the magnitude of the polarization can be measured as a function of increasing the terminal aliphatic chain length on the external side of the chiral center. As this extension is altered, the environment of the asymmetric carbon changes from being in a relatively terminal position to being buried within the overall structure. In the smectic state, the terminal positions of the molecules will have relatively free mobilities compared to internal locations that are closer to the core. Thus, when the chiral center has a freer mobility the coupling between the dipoles at the chiral center and those in the chiral environment will be weaker leading to a lower measured value of the spontaneous polarization, as is the case for the 1-methylpropyl homologue (see Fig. 6). On the other hand, for molecules where the chiral center lies in an internal location, the asymmetric center will have less mobility, e.g. as in the 1-methylheptyl member and hence the spontaneous polarization increases. Thus by progressively extending the external portion of the aliphatic chain while maintaining the location of the chiral center, the motion of the chiral center is expected to become damped. Therefore, as the external chain is extended, the spontaneous polarization increases because the full weight of

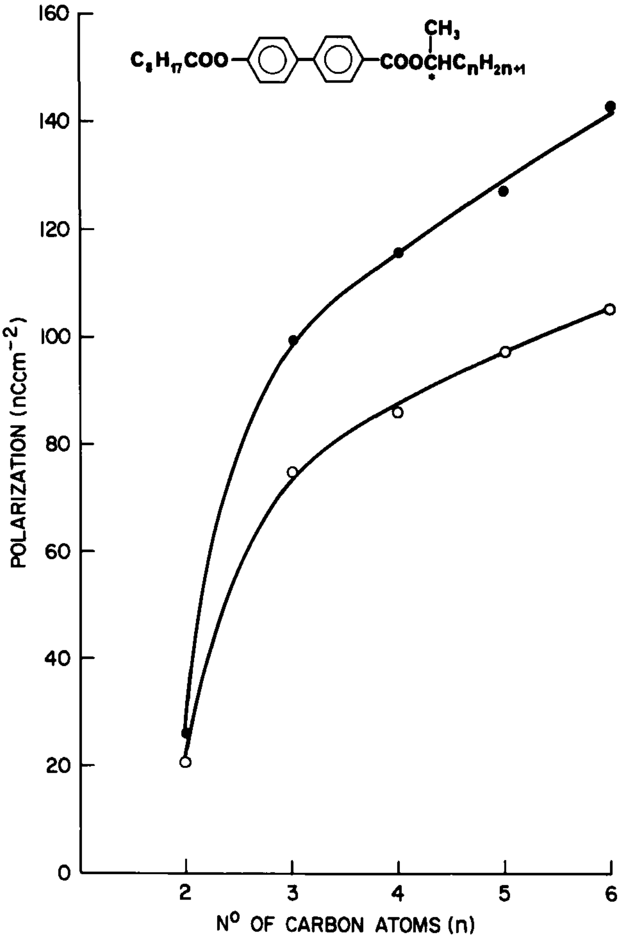


Fig. 6 The polarization (nC cm^{-2}) plotted as a function of increasing alkyl chain length for 1-methylalkyl 4-n-octanoyloxybiphenyl-4′-carboxylates. Key; ○, $T_{AC^*}-T = 10°C$; ●, $T_{AC^*}-T = 20°C$.

the dipole at the chiral center is being felt in couplings with the other dipoles in the chiral environment. The loss of the ferroelectric C* phase as the external chain is increased is similarly related to the increase in the steric interactions of the lateral methyl group at the chiral center. As the motion of the chiral center becomes damped, the lateral methyl branch will have stronger steric interactions with its neighboring molecules. This lateral disturbance would be expected to depress the formation of the smectic C* phase.

Thus, we can see from these results that there is a delicate balance to be maintained between steric and dipolar interactions in order to retain smectic C* properties. The strength of the dipole at the chiral center appears to strongly effect mesogenic morphology with a tendency for stronger dipoles to favor crystalline phases. On the other hand, stronger repulsive steric interactions tend to suppress the more ordered and tilted smectic phases completely. These results are in keeping with well-known studies on achiral systems.

CONCLUSION

In this study we have demonstrated that the local dipolar and steric interactions of the chiral center in a mesogenic material play a very important role in the stability of the ferroelectric C* phase. For instance, an increased dipole moment at the chiral center ($-Cl$ vs. $-CH_3$) and in the terminal chain (ether compounds) increases the repulsive dipolar interactions between neighboring molecules, leading to a suppression of tilted phases. In addition, strong off-axis steric effects, as in the methoxy or 1-methyheptyl compounds, increase steric interactions which in turn disturb the molecular packing sufficiently enough to depress the formation of the smectic C* phase.

Finally, although many of these materials do not exhibit C* phases, they may prove to be useful in tailoring the physical properties of ferroelectric liquid-crystalline mixtures.

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