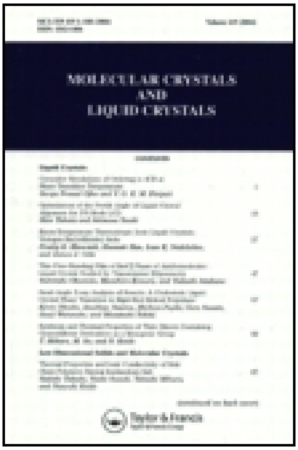

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# Liquid-Crystalline Derivatives of S-3,7-dimethyloctan-1-ol

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# Liquid-Crystalline Derivatives of S-3,7-dimethyloctan-1-ol

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A wide variety of liquid-crystalline derivatives of *S*-β-citronellol (*S*-3,7-dimethyloct-6-ene-1-ol) were prepared and found to exhibit ferroelectric smectic phases. The *S*-β-citronellol was initially hydrogenated to produce *S*-3,7-dimethyloctan-1-ol (3M7M8OH). This in turn was either brominated, oxidized, or used in an unchanged form to synthesize a range of materials, many of which exhibited smectic C* phases. The magnitude of the spontaneous polarization for a number of these derivatives was measured. Generally, the materials reported were found to have values for their spontaneous polarizations in the range of 5 to 15 $\mathrm{nCcm^{-2}}$. Many of the materials were also found to have short helical pitches in their C* phases, making them useful as unwinding agents in ferroelectric mixtures.

## INTRODUCTION

The synthesis of optically active smectogenic materials has increased considerably since the invention of a fast switching light-valve based on their ferroelectric properties.[1] Generally, in applications of nematic liquid crystals it is usual to mix various materials together in order to obtain a blend which has desirable properties for the proposed application. Similarly, in applications of ferroelectric smectogens the blending of various materials is required to control physical properties such as the temperature range of the phase, the size of the spontaneous polarization, and the pitch of the helical ordering of the molecules. This can be achieved in part by mixing materials which have the same or opposing spontaneous polarization directions and twist senses.[2,3,4]

Moreover, the magnitude of the spontaneous polarization for an individual material also depends critically on the nature and environment of the chiral center within the molecular structure of the smectogen itself.[5,6,7] Thus, the terminal chiral group assumes a dominating role in the optimization of material properties for applications. Consequently, the search for useful chiral substrates for the synthesis of novel ferroelectric smectogens is important.

This study presents data on liquid-crystalline analogues which contain the S-3,7-dimethyloctyl-moiety. The optical, ferroelectric and phase properties of the materials that were found to exhibit tilted smectic modifications were investigated.

## RESULTS AND DISCUSSION

### 1. Phase behavior

A number of derivatives of S-3,7-dimethyloctan-1-ol were prepared by first hydrogenating S-β-citronellol (Aldrich) in the presence of Adam's catalyst and then by brominating, oxidizing, or using the alcohol in its original form to produce benzoyloxybenzoate, phenylbenzoate, and biphenyl carboxylate derivatives.[8] The structures of these materials, their phase classifications, transition temperatures, and enthalpies of transition are given in Tables I to III inclusive. The transition temperatures as a function of increasing terminal n-alkoxy chain length for the homologous series (I) and (II) are listed in Tables I and II, and are shown in Figures 1 and 2 respectively.

A number of "liquid-crystalline trends" are immediately apparent from these results. Firstly, the S-3,7-dimethyloctyl-moiety raises the A to C* transition temperatures considerably in comparison to analogous S-2-methylbutyl derivatives. For example the A to C* transition temperatures are approximately 15° higher for the S-3,7-dimethyloctyl 4-n-alkoxybenzoyloxybenzoates in comparison to the S-2-methylbutyl 4-n-alkoxybenzoyloxybenzoates.[9] Secondly, when the chiral moiety is positioned at the opposite end of the core relative to the direction (or flow) of perturbations of the delocalized electrons in the aromatic core structure a cholesteric, smectic C* phase sequence is observed. When this structural arrangement is reversed a smectic A, smectic C* sequence is observed. This result is in agreement with

TABLE I

$(I)S\text{-}C_nH_{2n+1}OC_6H_4COOC_6H_4COO(CH_2)_2\overset{*}{C}H(CH_3)(CH_2)_3CH(CH_3)_2$

| n | Twist | Ps(sign) | m.p.[a] | Recryst.[a] | C*-A[b] | A-Iso[b] | C*-Iso |
|---|---|---|---|---|---|---|---|
| 7 | l(−) | (+) | 35.6 | 18.0 | – | 49.6 | – |
| $\Delta$H | – | – | (15.6) | (9.6) | – | (2.9) | |
| 8 | l(−) | (+) | 38.5 | 14.9 | 30.2 | 51.1 | – |
| $\Delta$H | – | – | (15.3) | (12.3) | (0.01) | (3.3) | |
| 9 | l(−) | (+) | 39.4 | 21.1 | 40.3 | 50.0 | – |
| $\Delta$H | – | – | (12.4) | (11.06) | (0.01) | (3.0) | |
| 10 | l(−) | (+) | 38.8 | 22.5 | 46.0 | 51.3 | – |
| $\Delta$H | – | – | (11.4) | (10.4) | (0.04) | (3.1) | |
| 11 | l(−) | (+) | 42.3 | 28.5 | 47.4 | 50.4 | – |
| $\Delta$H | – | – | (15.8) | (12.3) | (0.09) | (2.9) | |
| 12 | l(−) | (+) | 37.5 | 20.5 | 49.0 | 51.8 | – |
| $\Delta$H | – | – | (15.0) | (9.2) | (0.02) | (2.92) | |
| 13 | l(−) | (+) | 47.4 | 28.2 | 48.6 | 49.8 | – |
| $\Delta$H | – | – | (15.3) | (14.3) | (0.01) | (3.7) | |
| 14[c] | l(−) | (+) | 41.5 | 38.3 | 50.0 | 51.0 | – |
| $\Delta$H | – | – | – | – | – | – | – |
| 16 | l(−) | (+) | 48.3 | 28.9 | – | – | 49.7 |
| $\Delta$H | – | – | (19.7) | (15.54) | – | – | (3.2) |

Transition temperatures in °C.
Enthalpy values in cal/gm.
[a]Temperatures obtained by DSC.
[b]Temperatures obtained by thermal optical microscopy.
[c]Too little sample to measure enthalpies.
$C_6H_4$—is a 1,4-substituted phenyl ring.

previous observations,[10] and is classically demonstrated by comparing the isomeric pair of materials 1 and 2 shown in Table III. Thirdly tilted smectic phases are injected typically at n-alkoxy chain lengths which exceed six to eight carbon atoms in length.[9]

## 2. Phase classification

The phases exhibited by the materials were classified from their microscopic textures. The textures were obtained with the specimen contained between glass plates, or in an uncovered droplet, or in a free-standing film. A number of these materials were also subjected to miscibility studies using S-4-(2-methylbutyl)phenyl 4-n-octylbiphenyl-4′-carboxylate[10] (8SI or CE8(BDH Chemicals)) (Ch, A, C*, I*, J*, and G* phases) and S-4-hexyloxyphenyl 4-(4′-methylhexyl-

TABLE II

$(II)S\text{-}C_nH_{2n+1}OC_6H_4OCOC_6H_4OCOC_6H_4O(CH_2)_2\overset{*}{C}H(CH_3)(CH_2)_3CH(CH_3)_2$

| n | Twist | Ps(sign) | m.p.[a] | Recryst.[a] | C*-Ch[b] | Ch-Iso[b] |
|---|---|---|---|---|---|---|
| 6 | d(+) | (−) | 97.0 | 56.2 | 114 | 154.2 |
| ΔH | – | – | (15.66) | (11.6) | (0.87) | (0.43) |
| 7 | d(+) | (−) | 79.5 | 55.5 | 116.6 | 150.0 |
| ΔH | – | – | (11.8) | (9.1) | (0.89) | (0.34) |
| 8 | d(+) | (−) | 75.1 | 51.1 | 120.9 | 150.6 |
| ΔH | – | – | (11.63) | (7.4) | (0.81) | (0.43) |
| 10 | d(+) | (−) | 67.3 | 40.5 | 119.5 | 143.5 |
| ΔH | – | – | (10.9) | (8.1) | (0.94) | (0.4) |
| 11 | d(+) | (−) | 63.5 | 48.1 | 120.0 | 138.3 |
| ΔH | – | – | (9.2) | (9.4) | (1.02) | (0.41) |
| 12 | d(+) | (−) | 70.5 | 52.4 | 120.2 | 138.6 |
| ΔH | – | – | (8.1) | (10.7) | (0.86) | (0.36) |
| 14 | d(+) | (−) | 65.2 | 52.7 | 118.7 | 133.9 |
| ΔH | – | – | (7.6) | (10.5) | (0.79) | (0.38) |
| 16 | d(+) | (−) | 70.1 | 65.8 | 115.8 | 129.3 |
| ΔH | – | – | (14.2) | (14.7) | (0.6) | (0.38) |

Transition temperatures in °C
Enthalpy values in cal/gm
[a]Temperatures obtained by DSC
[b]Temperatures obtained by thermal optical microscopy
$C_6H_4$—is a 1,4-substituted phenyl ring

oxy)benzoyloxybenzoate[11] (Ch and C* phases) as the standard materials. The materials in Table I showed continuous miscibility with the A and C* phases of the standard material 8SI. Similarly the materials in Table II showed continuous miscibility with the cholesteric and C* phases of the second standard.

Unusual phase diagrams, however, were obtained when the S-4-n-alkoxyphenyl 4-(3′,7′-dimethyloctyloxy)benzoyloxybenzoates (II) (Ch and C* phases) were mixed with 8SI. The cholesteric phases of the test and standard materials were continuously miscible, but the smectic C* phases were not. At the point where the A phase disappears in the phase diagram a smectic B phase is injected disrupting the continuity of the C* phase, as shown in Figure 3. It appears that the C* phase of 8SI which has a low tilt angle and the C* phase of the benzoyloxybenzoate which has a high tilt angle are immiscible, i.e., the two tilts annihilate each other thus producing an orthogonal B phase.

TABLE III

| | Compound | Transition Temperatures | Twist Sense | Polarization Direction |
|---|---|---|---|---|
| 1. | S—$C_{10}H_{21}OC_6H_4COOC_6H_4O3M7M8$ | Iso-A, 60.3; A-C*, 49.4. | d | Ps(−) |
| 2. | S—$C_{10}H_{21}OC_6H_4OOCC_6H_4O3M7M8$ | Iso-Ch, 46.5; Ch-C*, 40.9. | d | Ps(−) |
| 3. | S—$C_{12}H_{25}OC_6H_4C_6H_4COO3M7M8E$ | Iso-A, 52.7; A-C*, 46.8. | l | Ps(+) |
| 4. | S—$C_{10}H_{21}OC_6H_4COOC_{10}H_6COOC_6H_4O3M7M8$ | Iso-Ch, 262; Ch-A, 259; A-C*, 257. | – | – |
| 5. | S—$C_{10}H_{21}OC_6H_4OOCC_{10}H_6OOCC_6H_4O3M7M8$ | Iso-Ch, 185; Ch-C*, 158. | – | – |
| 6. | S—$C_{14}H_{29}OC_6H_4COOC_6H_4CO2M6M7$ | Iso-A, 63.4; A-C*, 57.4. | l | Ps(+) |
| 7. | S—$C_8H_{17}OC_6H_4COOC_6H_4CO2M6M7$ | Iso-A, 173; A-C*, 138; C*-I*, 74. | l | Ps(+) |
| 8. | S—$C_{10}H_{21}C_6H_4C_6H_4COOC_6H_43M7M8$ | Iso-A, 120.5; A-C*, 104; C*-$S_3$, 68.5. | l | Ps(+) |

where 3M7M8 is 3,7-dimethyloctyl
2M6M7 is 2,6-dimethylheptyl
3M7M8E is 3,7-dimethylocta-6-enyl
$C_6H_4$ is a 1,4 substituted phenyl ring
$C_{10}H_6$ is a 2,6 substituted naphthalene ring system.

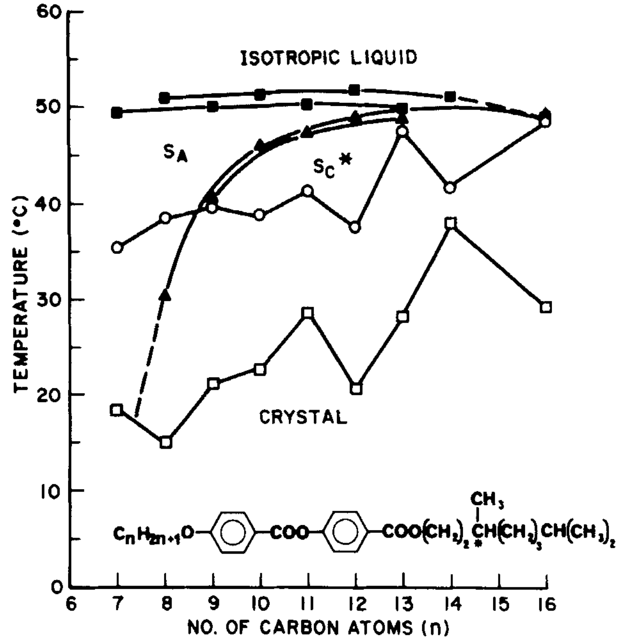

FIGURE 1 The transition temperatures of the S-3,7-dimethyloctyl 4-n-alkoxybenzoyloxybenzoates(I) shown as a function of increasing terminal n-alkoxy chain length: key, Iso-A, ●; A-C* or Iso-C*, ▲; crystal to mesophase on heating, ○; mesophase to crystal on cooling, □.

## 3. Optical properties

*a. Optical purity.* An important factor in generally assessing, normalizing, and comparing the properties of materials is knowing the relative amounts of the R and S optical isomers in typical samples of each material. In the case of the derivatives of S-3,7-dimethyloctan-1-ol the enantiomeric excesses of the final products are predetermined by the optical purity of the starting alcohol. The optical purity of S-3,7-dimethyloctan-1-ol was therefore determined by reacting it with (−)-mandelic acid to produce a mixture of diastereoisomers of 3,7-dimethyloctylmandelate. The relative proportions of each diastereoisomer in the esterified product is the same as for each optical isomer in the starting alcohol. Separation of the diastereoisomers was achieved analytically by reverse phase liquid chromatography. The relative optical purity for the S-3,7-dimethyloctan-1-ol determined by this method was greater than 0.96 ee, i.e., essentially only the S isomer is present.

*b. Helical twist direction.* The twist directions of the helical ordering of the molecules in the C* phases of the materials investigated were determined by the contact method against materials of known twist sense.[3] Most of the materials studied complied with the twist sense rules initated by Gray and McDonnell for cholesterics,[12] i.e., all are classified as Sol or Sed where S is the absolute configuration of the chiral center, o and e are the parity displacement of the chiral center from the aromatic core, and d and l are the rotations of plane polarized light through the liquid-crystalline medium. One exception to these rules was found and is demonstrated by compounds 6 and 7 of Table III. In both of these cases the terminal chiral group is separated from the aromatic core by a ketone function. The carbonyl group acts as part of the terminal off-axis aliphatic chain and therefore the parity has to be adjusted to take this into account. Once this is done these materials agree with the rules for cholesterics.[4]

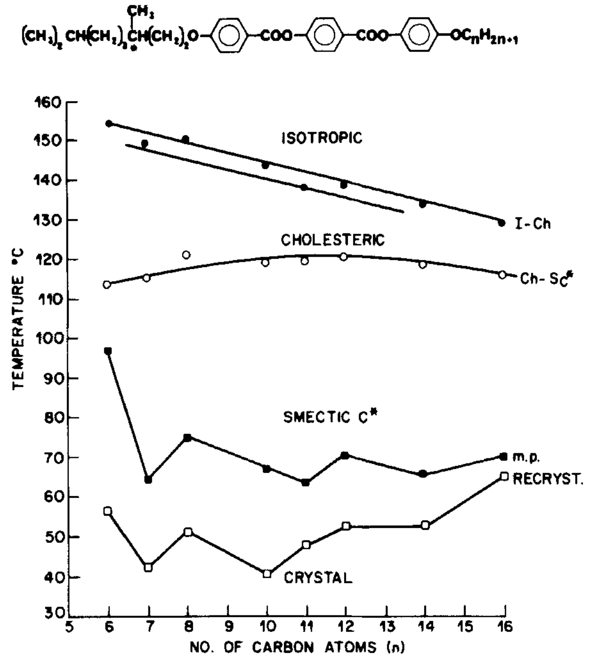

FIGURE 2 The transition temperatures of the S-4-n-alkoxyphenyl (4-(3′-7′-dimethyloctyloxy)benzoyloxybenzoates(II) shown as a function of increasing terminal n-alkoxy chain length: key, Iso-Ch, ●; Ch-C*, ○; crystal to mesophase on heating ●; mesophase to crystal or cooling, □.

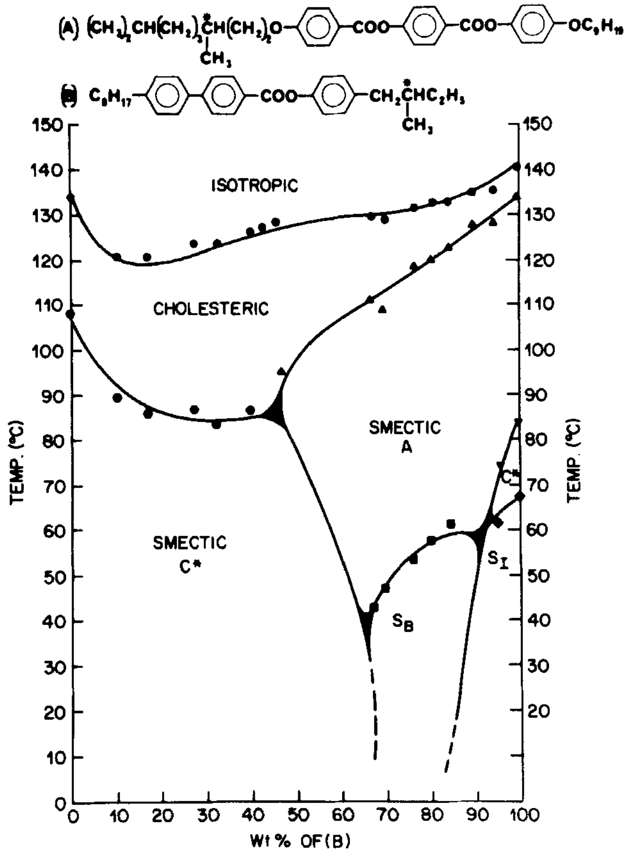

FIGURE 3 Miscibility diagram for binary mixtures (wt.%) of S-4-(2′-methylbutyl)phenyl 4-n-octylbiphenyl-4′-carboxylate (8SI), (B), and S-4-n-nonyloxyphenyl 4-(3′,7′-dimethyloctyloxy)benzoyloxybenzoate, (A).

*c. Pitch measurements.* The pitch of the helix for the macroscopic orientational ordering of the molecules in the C* phases of various materials was measured by optical methods using a calibrated Filar eyepiece. The results for the homologous series (I) at a reduced temperature of 5° below the A to C* phase transition are plotted against increasing terminal n-alkoxy chain length in Figure 4. This figure shows that the pitch does not increase monotonically as a function of increasing molecular length, but that a minimum pitch is obtained at approximately the n-dodecyloxy homologue. Two possible interpretations can be used to explain this behavior; either the azimuthal angle between the tilt orientation of successive layers in

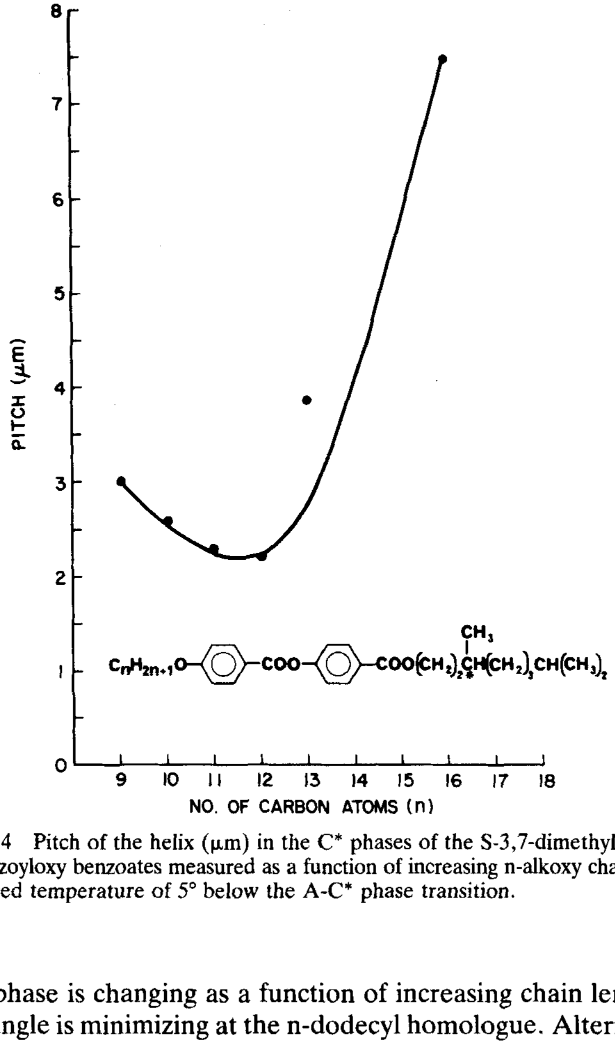

FIGURE 4 Pitch of the helix (μm) in the C* phases of the S-3,7-dimethyloctyl 4-n-alkoxybenzoyloxy benzoates measured as a function of increasing n-alkoxy chain length, at a reduced temperature of 5° below the A-C* phase transition.

the C* phase is changing as a function of increasing chain length, or the tilt angle is minimizing at the n-dodecyl homologue. Alternatively both mechanisms could be occurring concurrently.

It is also interesting to note that this minimization in the pitch occurs at approximately the same n-alkoxy chain length as the A to C* transition temperatures are maximized in the homologous series.

*d. Optical tilt angle measurements.* Optical tilt angle measurements as a function of reduced temperature below the A to C* phase transition were made on a number of the materials as described previously.[3] Typically materials that exhibited a Ch, C* phase sequence (series II) were found to have a high saturated optical tilt angle in the C* phase. For a majority of the materials studied this angle was found to be approximately 45°. Materials that exhibited an A, C* sequence (series I and Table III), however, usually possessed saturated optical tilt angles below 25°.

Moreover, in series (I) the optical angle was measured at a reduced temperature of 5° below the A to C* phase transition for all of the members that were synthesized. The results were remarkably consistant varying between 19 and 21° for all of the homologues. With respect to the experimental error, the members had essentially the same optical tilt angle. Results over a wider temperature range for the n-undecyloxy and n-dodecyloxy homologoues are shown together in Figure 5. Again the differences in tilt angle between the two materials are essentially within the experimental error (±1°). Similar results were also obtained for the analogous S-2-methylbutyl 4-n-alkoxybenzoyloxybenzoates which also showed optical tilt angles of

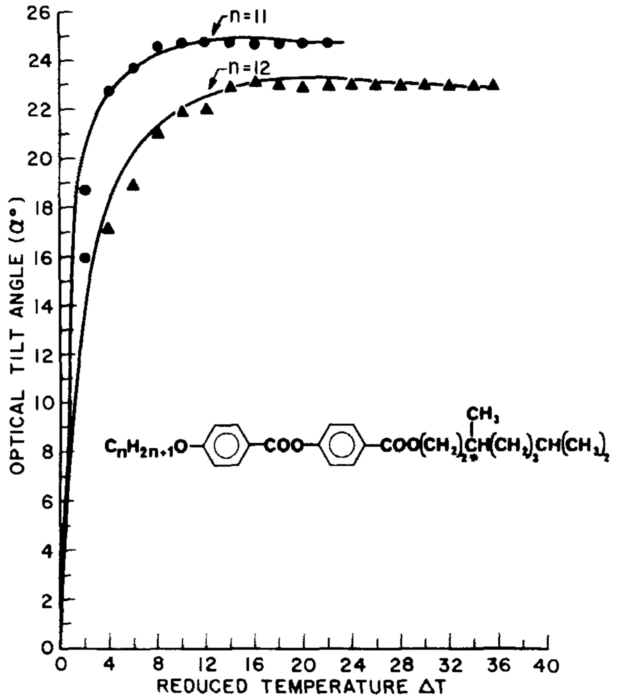

FIGURE 5 The optical tilt angle in degrees measured as a function of reduced temperature below the A-C* phase transition for S-3,7-dimethyloctyl 4-n-undecyloxybenzoyloxybenzoate (n = 11) and S-3,7-dimethyloctyl 4-n-dodecyloxybenzoyloxy benzoate (*n* = 12).

between 19 and 21° at a temperature of 5° below the A to C* phase transition.

One possible explanation of these results is that the drive to form the C* phase may be dominated by the interactions of the core, because the optical tilt angle is essentially a measure of the tilt of the aromatic core with respect to the layer planes. As the optic tilt angle does not vary much from member to member, the local interactions between the cores could be stabilizing a preferred tilted structure of the cores in a particular orientation irrespective of the position and length of the terminal chains.[13] Thus, the overall tilt angle may change from member to member in these homologous series as the terminal-chain length is varied, but the tilt of the core remains relatively fixed.

## 4. Polarization studies

*a. Sign of the spontaneous polarization.* The sign of the spontaneous polarization for materials which exhibit A and C* phases was determined by electrical field studies as described previously.[3] The signs found for each individual material are listed in Tables I and III. For materials which exhibit choelsteric and C* phases the sign was determined by using an alignment method for the C* phase described previously,[14] and assuming a polar surface interaction, which requires that the polarization points into the surface of the cell. Again switching studies in a DC field are used to determine the polarization direction. The results obtained for these materials are listed in Tables II and III.

A simple conclusion which can be drawn from the data presented in these tables is that the polarization has the opposite sign to the twist direction. This result is in agreement with data obtained previously.[2,3]

*b. Magnitude of the spontaneous polarization.* The size of the polarization for various S-3,7-dimethyloctyl homologues was measured by methods described previously.[15-17] The results obtained for seven compounds are shown in Figures 6 to 8 inclusive. The polarizations for four compounds that exhibit A and C* phases are compared in Figure 6 as a function of reduced temperature below the A to C* phase transition. Three different aromatic core structures are depicted which possess varying degrees of electronegativity associated with the dipolar, functional groups (e.g., COO) contained within their structures. The measured polarizations do not appear to be effected greatly by the number of these groups included in the system. Thus

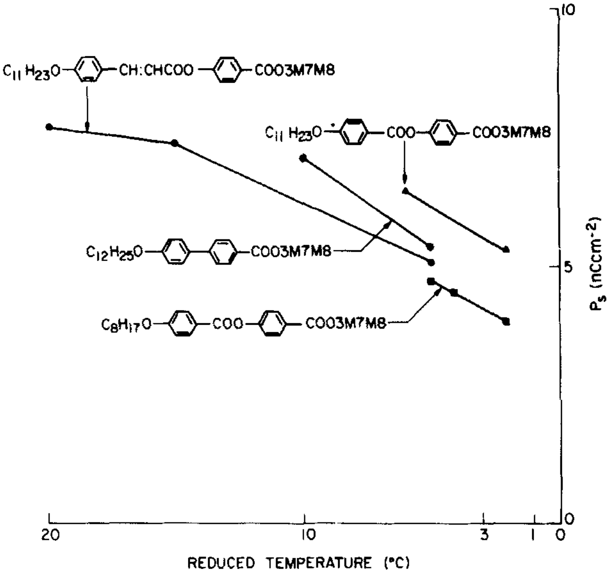

FIGURE 6 The spontaneous polarization (nCcm$^{-2}$) measured as a function of reduced temperature for S-3,7-dimethyloctyl 4-n-octyloxybenzoyloxybenzoate, S-3,7-dimethyloctyl 4-n-undecyloxybenzoyloxybenzoate, S-3,7-dimetylocta-6-enyl 4-n-dodecyloxybiphenyl-4′-carboxylate, and S-3,7-dimethyloctyl 4-n-undecyloxycinnamoyloxybenzoate.[9]

the spontaneous polarization does not seem to be dependent on the extent of the polarity of the core which usually contains the stronger dipolar groups that make up the molecular dipole moment of the system. In fact when the polarizations of the homologous n-octyl and n-undecyloxy benzoyloxybenzoates are compared, they show almost as greater difference in magnitude within a homologous series as that which is observed between the different series. This result indicates the relative insensitivity of the spontaneous polarization in a variety of different systems which contain the same chiral functionality.

A comparison of the results for high and low tilt smectic C* variants are shown in Figure 7 for the isomeric compounds 1 and 2 (Table III). These two compounds differ structurally only by the direction of the central ester linkage. One compound has a cholesteric, C* phase sequence with a saturated optical tilt in the C* phase of approximately 45°, whereas the other exhibits an A, C* sequence with a saturated optical tilt in the C* phase of approximately 25°. The dipolar properties of the two materials are almost equivalent, however, the spontaneous polarization of the high tilt material is almost twice the size of the low tilt substance at the same reduced temper-

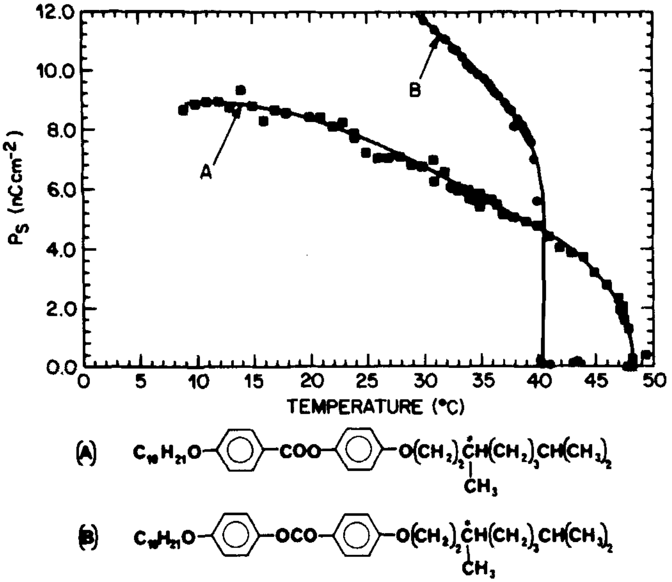

FIGURE 7 The spontaneous polarization (nCcm$^{-2}$) measured as a function of reduced temperature for the two isomeric compounds S-3,7-dimethyloctyloxyphenyl 4-n-decyloxybenzoate (A) and S-4-n-decyloxyphenyl (4-(3′,7′-dimethyloctyloxy) benzoate (B).

ature. This result indicates that the spontaneous polarization of a system is highly sensitive to the magnitude of the tilt angle.

The last figure (8) shows the polarization measurements for S-4-n-heptyloxyphenyl 4-(3′,7′-dimethyloctyloxy)benzoyloxybenzoate which possesses cholesteric and C* phases. The C* phase has a high optical tilt angle of approximately 45°, and instead of the polarization rising and then levelling off as with the other materials reported, this time it continues to rise as the temperature is lowered. This is the reverse of the usually predicted course for the polarization in smectics, however, this result is typical of many of the compounds that we have recently studied. Extrapolated values for these materials can be extremely high at room temperature, yet it remains to be seen whether these materials will produce similar effects in eutectic mixtures.

## EXPERIMENTAL

The compounds were prepared by standard methods involving protection and deprotection techniques.[8] The purities of the materials were determined by reverse phase liquid chromatography using a

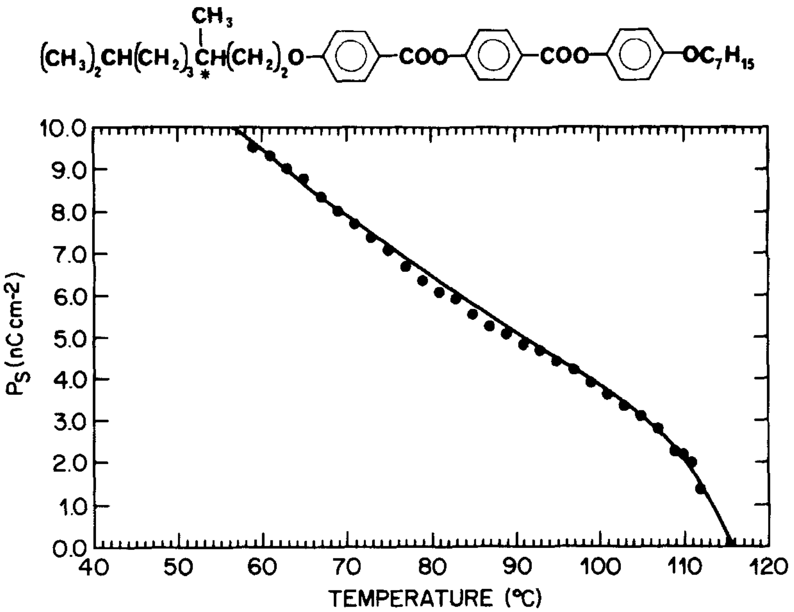

FIGURE 8 The spontaneous polarization (nCcm$^{-2}$) measured as a function of reduced temperature for S-4-n-heptyloxyphenyl 4-(3′,7′-dimethyloctyloxy)benzoyloxybenzoate.

Beckmann 344 system in conjunction with a UV-Vis variable wavelength detector, and an octadecylsiloxane (5 μm, 25 × 0.46 cm) column. The structures of the final products were elucidated by IR, NMR, and mass spectrometry, the results for which were in agreement with the predicted structures.

Transition temperatures were determined by thermal optical microscopy using a Zeiss Universal Microscope in conjunction with a Mettler FP52 microfurnace and control unit, and by differential scanning calorimetry using a Perkin-Elmer DSC-4-TADS system.

Optical switching and twist sense studies were made as described previously.[3] Spontaneous polarizations were measured by two different methods which gave compatible results with one another.[15-17]

## SUMMARY

The S-3,7-dimethyloctyl-chiral moiety was shown to be useful in broadening the smectic C* range when included in certain liquid-crystalline systems. The optical purity of the starting alcohol is extremely good making the normalization of the results for various properties unnecessary. The measured spontaneous polarizations for the materials are comparable to those obtained for the S-2-methylbutyl analogues, making these compounds useful for mixture purposes.

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