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The effect of structural changes in the molecular core and periphery on the liquid-crystalline properties of some chiral 4-*n*-alkoxyphenylpropiolates

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The effect of structural changes in the molecular core and periphery on the liquid-crystalline properties of some chiral 4-*n*-alkoxyphenylpropiolates

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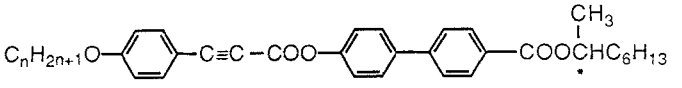
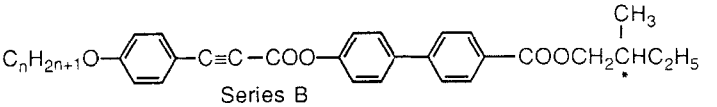
The thermotropic liquid-crystalline properties of several homologous series of chiral 4-*n*-alkoxyphenylpropiolates were correlated with chemical structural modification on the periphery of the rigid, aromatic, molecular core. The temperature ranges of the most disordered mesophase in each series were shown to be inversely proportional with respect to the number of carbon atoms in the terminal alkoxy moiety. The type of mesophase exhibited by an homologous series is determined by the number of carbons in the chiral alkyl substituent. Homologous series containing short chain chiral alkyl substituents formed mesophases that had higher degrees of disorder (i.e. cholesteric phases) than did those that contained long chain chiral alkyl substituents.

1. Introduction

We recently reported the discovery and characterization of a new liquid crystal modification, the helical smectic A phase [1]. This phase appears in a homologous series of (*R*) and (*S*)-2-octyl 4′-[(4″-*n*-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates that have the general structure shown in series **A**. This new mesophase is also expected to occur in materials that are structurally similar to **A**. Hence, we have prepared the homologous series of (*S*)-2-methylbutyl 4′-[(4″-*n*-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates (phenylpropiolates), having the general structure shown in series **B**.

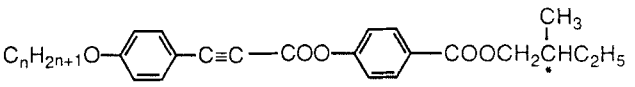


Series A

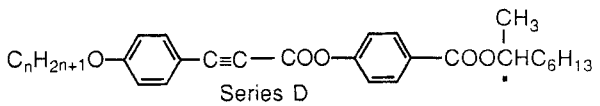


Series B

* Author for correspondence.



Series C



Series D

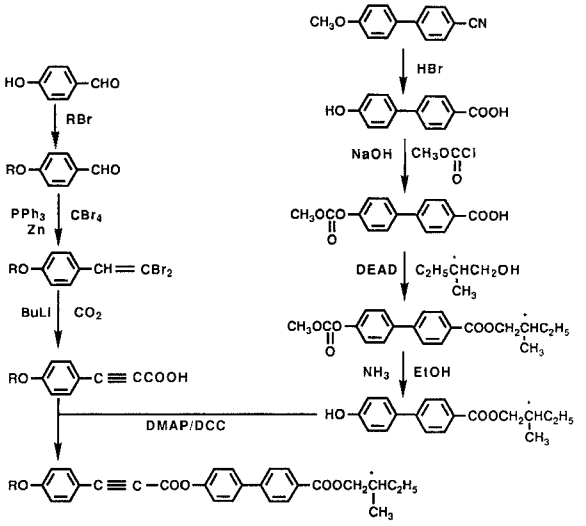
In this article the thermotropic behaviour of this new series and related phenylpropiolates (series **C** and **D**) is reported. In addition, the effect of structural changes in the molecular core and molecular periphery of the materials was investigated and correlated with the formation of the incipient liquid-crystalline phase.

2. Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Transition temperatures were determined by thermal, polarized-light microscopy using a Zeiss Universal polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP5 control unit. Similarly, the enthalpies and temperatures of transition were determined by differential scanning calorimetry using a Perkin–Elmer DSC 4-TADS system. Infrared spectra were obtained using a Perkin–Elmer 1320 or a Perkin–Elmer 238 Infrared Spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Nicolet NT 200, General Electric QE-300, Bruker 370, or a Jeol 400-GX NMR Spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS). Mass spectra were obtained using a Finnigan Mat 4500B EI/CI Mass Spectrometer System or a Hewlett Packard System. The term concentrated refers to removal of solvent under reduced pressure with a rotary evaporator. All commercially available reagents were used without further purification unless otherwise indicated. Tetrahydrofuran and anhydrous ether were purified by distillation from sodium and benzophenone.

A general method for preparing the (*S*)-2-methylbutyl 4′-[(4″-*n*-alkoxyphenyl)propioloxy]biphenyl-4-carboxylates (series **B**) is shown in the Scheme. The 4-*n*-alkoxyphenylpropiolic acids were prepared by adapting a method previously reported by Corey and Fuchs [2]. 4-Hydroxybenzaldehyde was alkylated in the presence of potassium carbonate with an appropriate *n*-alkylhalide dissolved in acetone. The isolated 4-*n*-alkoxybenzaldehydes were purified by distillation under reduced pressure. The aldehydes were subjected to modified Wittig reactions with carbon tetrabromide in the presence of triphenylphosphine and zinc. This resulted in the formation of the analogous β,β-dibromostyrenes. When treated with *n*-butyllithium and carbon dioxide the styrenes afforded the analogous 4-*n*-alkoxyphenylpropiolic acids.

The (*S*)-2-methylbutyl 4′-hydroxybiphenyl-carboxylate was prepared from 4-methoxy-4′-cyanobiphenyl by hydrolysis and demethylation in one step to produce 4′-hydroxybiphenyl-4-carboxylic acid. This acid was then protected with methylchloroformate to give 4′-methoxycarbonyloxybiphenyl-4-carboxylic acid. This acid was esterified with (*S*)-2-methylbutanol in the presence of diethylazodicarboxylate (DEAD) to give (*S*)-2-methylbutyl-4′-methoxycarbonyloxybiphenyl-4-carboxylate. The protecting group was then removed by stirring the ester in a mixture of concentrated



ammonia and ethanol to yield (*S*)-2-methylbutyl 4′-hydroxybiphenyl-4-carboxylate. This biphenol was esterified with each 4-*n*-alkoxyphenylpropiolic acid, as we now describe, to give the appropriate members of series **B**.

2.1. *Preparation of 4′-[(S)-2-methylbutyl] 4-biphenylcarboxylate esters of 4-n-alkoxyphenyl-propiolic acids (series **B**)*

The following general procedure, which was adapted from the literature [3], was used. A solution containing 4-*n*-alkoxyphenylpropiolic acid (3 mmol), 4′-(*S*)-2-methylbutyl] 4-hydroxybiphenylcarboxylate [4] (3 mmol), and THF (50 ml) was added dropwise to a solution containing 1,3-dicyclohexylcarbodiimide (3 mmol), 4-dimethylaminopyridine (0·5 mmol) and THF (25 ml). The resulting mixture was stirred at room temperature for 6 h. The reaction mixtures was then filtered and concentrated. The resulting viscous residue was purified by flash chromatography (ether–hexane (5 : 95 v/v)) giving the 4-*n*-alkoxyphenylpropiolate in 65–70 per cent yield.

4-*n*-octyloxyphenylpropiolate; 70 per cent yield; IR (nujol) 2210, 1720, 1280, 1115, 1009, 837, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8·13 (2 H, d), 7·68 (6 H, m) 7·31 (2 H, d), 6·92 (2 H, d), 4·29 (2 H, m), 4·01 (2 H, t) 1·88–1·75 (3 H, overlapping peaks), 1·71–1·22 (12 H, overlapping peaks), 1·01 (6 H, m), 0·88 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 145·6°C; cholesteric to smectic A 108°C; smectic A to chiral smectic C, 70·5°C; recrystallization, 54·5°C; m.p., 80·1°C.

4-*n*-nonyloxyphenylpropiolate; 69 per cent yield; IR (nujol) 2200, 1727, 1268, 1130, 1015, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8·13 (2 H, d), 7·68 (6 H, m), 7·35 (2 H, d), 6·92 (2 H, d) 4·26 (2 H, m) 4·01 (2 H, t), 1·87–1·72 (3 H, overlapping peaks), 1·61–1·10 (15 H, overlapping peaks), 1·13–0·79 (9 H, overlapping peaks); transition temperatures; isotropic liquid to cholesteric, 144·2°C; cholesteric to smectic A, 116·6°C; smectic A to chiral smectic C, 80·5°C; recrystallization, 58·2°C; m.p., 72·2°C.

4-*n*-decyloxyphenylpropiolate; 68 per cent yield; IR (nujol) 2199, 1706, 1265, 1148, 828, 728 cm^{-1}, ^1H NMR ($CDCl_3$) δ 8·14 (2 H, d), 7·61 (6 H, m), 7·31 (2 H, d), 6·90 (2 H, d), 4·18 (2 H, m), 3·99 (2 H, t), 2·00–1·70 (3 H, overlapping peaks), 1·58–1·22 (14 H, overlapping peaks), 0·90 (6 H, crude t), 0·88 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 142·0°C; cholesteric to smectic A, 122·5°C; smectic A to chiral smectic C, 89·6°C; recrystallization, 69·3°C; m.p., 81°C.

4-*n*-undecyloxyphenylpropiolate; 65 per cent yield, IR (nujol) 2198, 1705, 1210, 1158, 827 cm^{-1}; ^1H NMR ($CDCl_3$), δ 8·13 (2 H, d), 7·66 (4 H, m), 7·56 (2 H, d), 7·28 (2 H, d), 6·90 (2 H, d), 4·21 (2 H, m), 3·99 (2 H, t), 1·84 (3 H, m), 1·60–1·22 (18 H, overlapping peaks), 1·00 (6 H, m), 0·84 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 140·8°C; cholesteric to smectic A, 123·2°C; smectic A to chiral smectic C, 94·4°C; recrystallization, 69·4°C; m.p., 80·2°C.

4-*n*-dodecyloxyphenylpropiolate; 70 per cent yield; IR (nujol) 2199, 1705, 1270, 1145, 828 cm^{-1}; ^1H NMR ($CDCl_3$)) δ 8·12 (2 H, d), 7·65 (4 H, m), 7·58 (2 H, d), 7·28 (2 H, d), 6·90 (2 H, d), 4·02 (2 H, t), 1·95–1·73 (3 H, overlapping peaks), 1·55–1·22 (20 H, overlapping peaks), 0·90 (6 H, crude t); transition temperatures; isotropic liquid to cholesteric, 136·0°C; cholesteric to smectic A, 125·7°C; smectic A to chiral smectic C, 94·0°C; recrystallization, 75·5°C; m.p., 84°C.

4-*n*-tridecyloxyphenylpropiolate; 68 per cent yield, IR (nujol) 2195, 1705, 1270, 1147, 828, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8·11 (2 H, d), 7·65 (4 H, m), 7·58 (2 H, d), 7·28 (2 H, d), 6·90 (2 H, d), 4·20 (2 H, m), 3·99 (2 H, t, 1·93–1·72 (3 H, overlapping peaks), 1·48–1·22 (22 H, overlapping broad peaks), 1·00 (6 H, m), 0·88 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 132·3°C; cholesteric to smectic A, 126·0°C; smectic A to chiral smectic C, 98·2°C; recrystallization, 70·4°C; m.p., 81·5°C.

4-*n*-tetradecyloxyphenylpropiolate; 70 per cent yield; IR (nujol) 2199, 1705, 1265, 1145, 1105, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8·12 (2 H, d), 7·65 (4 H, m), 7·58 (2 H, d), 7·29 (2 H, d), 6·90 (2 H, d), 4·19 (2 H, m), 3·99 (2 H, t, 1·95–1·73 (3 H, overlapping peaks), 1·64–1·22 (24 H, overlapping peaks), 1·04 (6 H, m), 0·84 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 131°C; cholesteric to smectic A, 125·3°C; smectic A to chiral smectic C, 98·3°C; recrystallization, 60·8°C; m.p., 76·6°C.

4-*n*-hexadecyloxyphenylpropiolate; 66 per cent yield, IR (nujol) 2198, 1705, 1270, 1149, 828, 770 cm^{-1}, ^1H NMR ($CDCl_3$) δ 8·11 (2 H, d), 7·65 (4 H, m), 7·57 (2 H, d), 7·28 (2 H, d), 6·90 (2 H, d), 4·20 (2 H, m), 0·99 (2 H, t), 1·92–1·74 (3 H, overlapping peaks), 1·57–1·23 (28 H, overlapping peaks), 0·99 (6 H, m), 0·88 (3 H, crude t); transition temperatures; isotropic liquid to cholesteric, 127·3°C; cholesteric to smectic A, 127·3°C; smectic A to chiral smectic C, 100·9°C; recrystallization, 53·0°C; m.p., 73·7°C.

3. Results

The (*S*)-2-methylbutyl 4′-[4″-*n*-alkoxyphenyl(propioloyloxy)]biphenyl-4-carboxylate homologues prepared are shown in the table (series **B**). The transition temperatures, enthalpy changes (ΔH), and phase temperature ranges (ΔT) for these compounds (series **B**) are also listed in the table. In figure 1 the transition temperatures for series **B** are plotted as a function of the carbon chain length in the *n*-alkoxy substituent.

Each of the homologues exhibits an isotropic liquid to cholesteric transition. The temperature at which the cholesteric phase appeared decreased in a typical sequential manner for series of this type as the chain length of the *n*-alkoxy substituent was increased. For the cholesteric to smectic A transition, the opposite trend was observed. The net cumulative effect of these two trends is shown in figure 2, where the absolute temperature range of the cholesteric (ΔT_{Ch}) mesophase is plotted as a function of the carbon chain length in the *n*-alkoxy substituent. From this graph, the temperature range (thermal stability) of the cholesteric phase was shown to decrease as the length of *n*-alkoxy substituent increased. For example, in the *n*-octyloxy derivative ΔT_{Ch} equals 27°C, but in the *n*-tetradecyloxy homologue ΔT_{Ch} is reduced to 5·7°C. For the

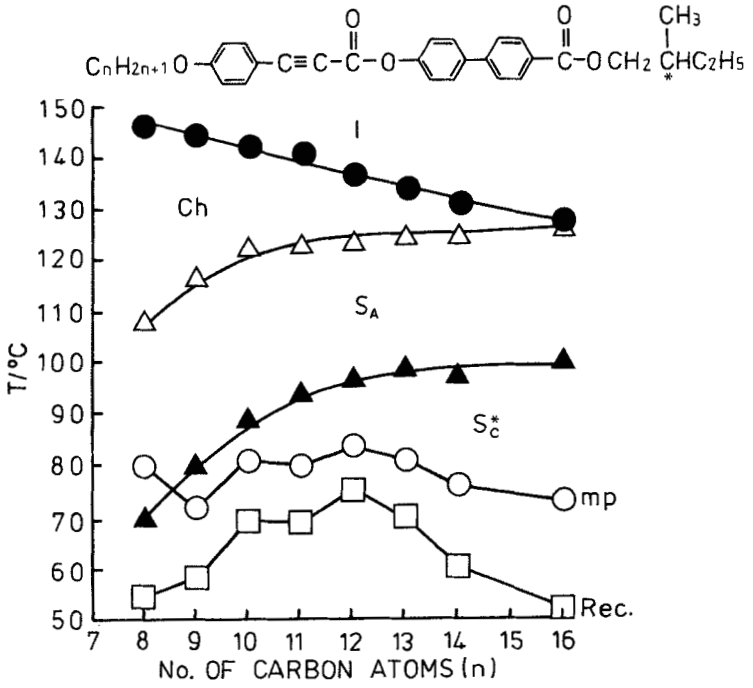


Figure 1. Plot of the transition temperatures for (*S*)-2-methylbutyl 4′-[(4″-*n*-alkoxyphenyl)-propioloyloxy]biphenyl-4-carboxylates (Series **B**) as a function of the number of carbons in the *n*-alkoxy chain.

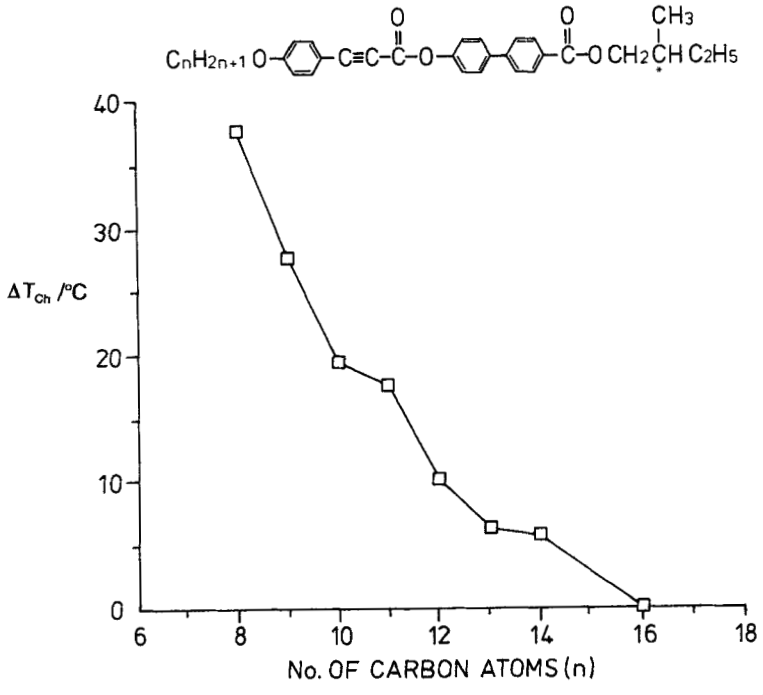
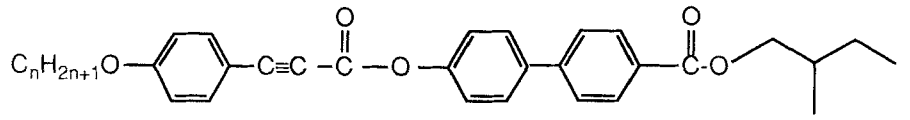


Figure 2. Plot of absolute temperature range ΔT_{Ch} for the cholesteric phase versus the number of carbons in the *n*-alkoxy chain of Series **B**.

Phase transition temperatures for 4′-[(*S*)-2-methylbutyl]-4-biphenylcarboxylate esters of 4-*n*-alkoxyphenylpropiolic acid(s).



n	m.p./°C	I→Ch/°C	ΔT_{Ch}/°C	Ch→S_A/°C	S_A→S_C/°C	Rec./°C
8	80·1 [40·9]	145·6 [0·13]	37·6	108·0 [0·16]	(70·5) [a]	54·5
9	72·2 [33·7]	144·2 [1·04]	27·6	116·6 [0·16]	80·5 [a]	58·2
10	81·0 [36·5]	142·0 [0·95]	19·5	122·5 [0·45]	89·6 [a]	69·3
11	80·2 [37·7]	140·8 [0·95]	17·6	123·2 [0·41]	94·4 [a]	69·4
12	84·0 [39·4]	136·0 [1·02]	10·3	125·7 [0·42]	94·0 [a]	75·5
13	81·5 [39·4]	132·3 [1·12]	6·3	126·0 [0·87]	98·2 [a]	70·4
14	76·6 [39·0]	131·0 [1·07]	5·7	125·3 [1·28]	98·3 [a]	60·8
16	73·7 [35·9]	127·3 [1·49]	0	127·3 [1·23]	100·9 [a]	53·0

( ), Monotropic phase; [ ], ΔH values kJ mol^{-1}; [a], ΔH value too small to be measured.

n-hexadecyloxy homologue the cholesteric phase has only a fleeting existence and appears to coexist with the smectic A phase. Examination of this derivative by optical microscopy shows that both the cholesteric and smectic A phases appear (sequentially) at 127·3°C. Differential scanning calorimetry confirmed that these two phases are separated by less than 2°C as indicated by the substantial overlap of the cholesteric and smectic A phase transition peaks.

Unfortunately, unlike series **A**, no twisted S_A phase was observed in the (*S*)-2-methylbutyl analogues, series **B**. This can be explained to some degree by examining the values of the enthalpies of the liquid crystal transitions as a function of the peripheral *n*-alkoxy chain length. We find for the clearing point enthalpies (Ch–I) that the values fall until the mid-point of the series is reached and then increase again. The situation for the cholesteric to smectic A transition is simpler in that the enthalpies only rise as the alkoxy chain is extended (see the table). Conversely for series **A** which exhibits twisted S_A phases, the clearing point transition enthalpies drop dramatically as the series is ascended [1] and only increase again when the nature of the phase transition changes from I–S_A to I–S_C^*. Thus the 2-methylbutyl series does not meet the criteria for exhibiting twisted S_A phases, which is that the transition to the S_A phase must tend towards being second order in nature as the series is ascended [5].

Each homologue of series **B** was also found to exhibit a smectic A to chiral smectic C phase transition. The chiral smectic C phase is enantiotropic for each member except for the *n*-octyloxy derivative for which it is monotropic. The average temperature range of the chiral smectic C phase is 20°C and did not appear to change substantially with an increase in the chain length of the *n*-alkoxy substituent.

Optical rotation studies were carried out on free-standing films while in the helical smectic C phase. Each of the homologues was found to have a left-hand helical structure (LH = dextro *d*) by this method. As the absolute spatial configuration of each homologue is *S*, the materials conform to the typical *Sed* classification for chiral materials. Moreover, switching studies also showed that the materials have negative polarization signs ($P_s(-)$), as predicted previously [6].

4. Discussion

Not surprisingly, the twisted smectic A phase was unobserved in homologous series **B**; this may be because of the reduced chirality of the series relative to series **A** and the higher values for the enthalpies of transition. However, the DSC and optical microscopy data obtained for series **B** in conjunction with the analogous data obtained for other related homologous series of phenylpropiolates provides for the correlation of subtle changes in the molecular structure of the 4-*n*-alkoxyphenylpropiolates with the thermal properties of the observed liquid-crystalline phases. In this respect it was found that the mesophase thermal stability was determined typically by the length of the *n*-alkoxy substituent and the length of the chiral alkyl substituent.

We also examined the thermotropic liquid-crystalline properties of three other closely related homologous series of phenylpropiolates; the (*S*)-2-octyl 4′-[(4″-*n*-alkoxyphenyl)-propioloyloxy]biphenyl-4-carboxylates (series **A**) [1], the (*S*)-2-methylbutyl 4-[(4′-*n*-alkoxyphenyl)propioloyloxy)]benzoates (series **C**) [7], and the (*S*)-2-octyl 4-[(4′-*n*-alkoxyphenyl)propioloyloxy]benzoates (series **D**). The transition temperatures for series **A** and series **C** are plotted as a function of the carbon chain length in the alkoxy substituent in figures 3 and 4, respectively. Comparisons of series **A**, **B** and **C** show that the first set of compounds, **A**, have a strongly diminishing smectic A temperature range with respect to an increasing terminal alkoxy chain length, as shown in figure 5. For series **C** the smectic A phase actually widens at longer chain lengths, whereas in series **B** the smectic A temperature range remains relatively constant as the series is ascended. For materials of this type to exhibit twisted S_A phases, the A phase must experience fluctuations from adjacent phases. Clearly in series **A** this is the case because as the S_A range diminishes the S_A phases feel stronger fluctuations from the adjacent S_C^* and isotropic phases. In the other series **B** and **C** this is not the case as the S_A phase always has a relatively large temperature range for each homologue.

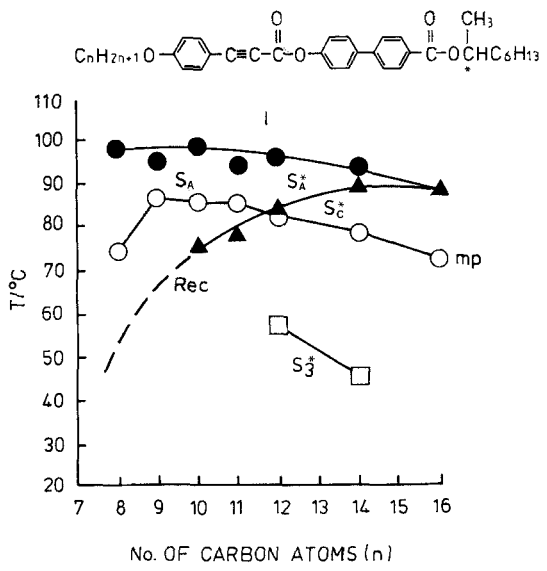


Figure 3. Plot of the transition temperatures for (*R*) and (*S*)-1-methylheptyl 4′-[(4″-*n*-alkoxyphenyl)propioloyloxy]biphenyl-4-carboxylates (Series **A**) as a function of the number of carbons in the *n*-alkoxy chain.

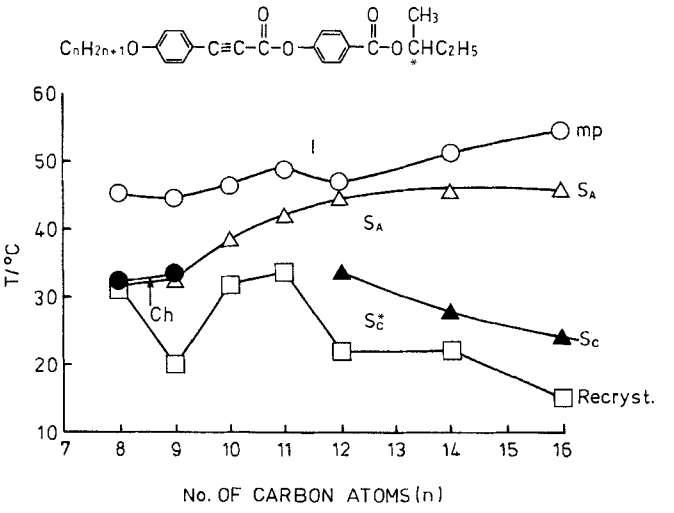


Figure 4. Plot of the transition temperatures for (*S*)-2-methylbutyl 4-(4′-*n*-alkoxyphenyl) propioloyloxy]benzoates (Series **C**) as a function of the number of carbons in the *n*-alkoxy chain.

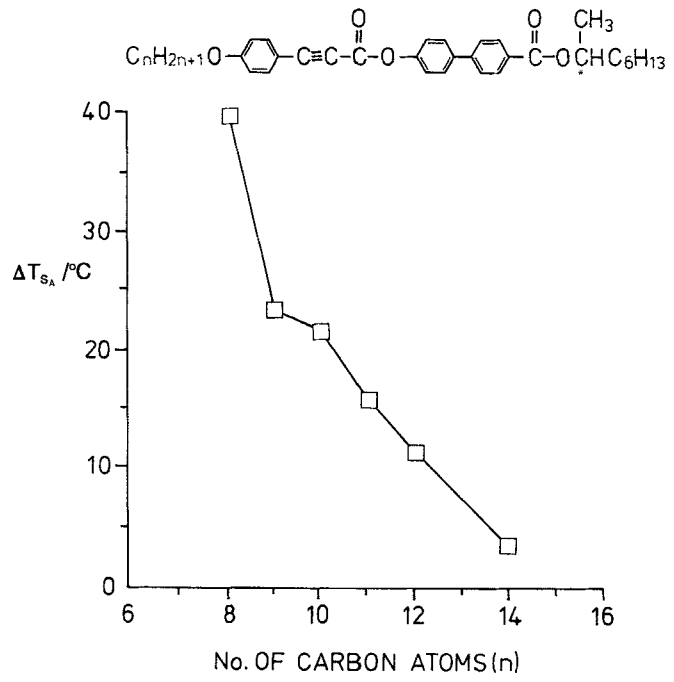


Figure 5. Plot of absolute temperature range ΔT_{S_A} for the smectic A phase versus the number of carbons in the *n*-alkoxy chain for Series **B**.

Thus, the results obtained for these three sets of materials appear to support de Gennes' [5], and Renn and Lubensky's [8] theories; that a second order phase transition with associated strong fluctuations from adjacent phases is required for the twist grain boundary phase to be stabilized.

Series **D** was also prepared in order to see if the twisted S_A phase could be obtained at lower temperatures than in the three ring analogues, series **A**. Unfortunately, because of recrystallization problems the appropriate phase morphology could not be obtained in this series in order to examine the formation of the twisted S_A phase. In fact series **D** showed no liquid crystal phases at all. Thus, the results on the four homologous series show how sensitive liquid crystal phase formation is to subtle changes in molecular structure.

5. Conclusion

A homologous series of (*S*)-2-methylbutyl 4′-[(4″-*n*-alkoxyphenyl) propioloyloxy]biphenyl 4-carboxylates was prepared *via* condensation of 4-*n*-alkoxyphenylpropiolic acids with a chiral biphenol moiety. DSC and thermal optical microscopy showed that these compounds were liquid-crystalline and each homologue exhibited the cholesteric, chiral smectic C, and/or the smectic A mesophase. The helical smectic A mesophase was not observed, suggesting that a high degree of chirality is required for this phase to be stabilized (as in the 2-octyl derivatives).

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