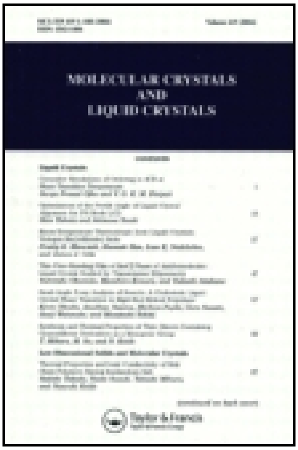

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Some Effects of Small Changes in Molecular Framework on the Incidence of Smectic C and Other Smectic Liquid Crystal Phases in Esters

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Some Effects of Small Changes in Molecular Framework on the Incidence of Smectic C and Other Smectic Liquid Crystal Phases in Esters†

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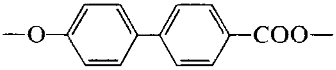
The smectic properties are discussed for several series of esters which have the same "central core" molecular structure, i.e.,



The effects of just extending the carbon chain in a series of n-alkyl esters are discussed for the methyl to n-decyl esters of 4′-n-decyloxybiphenyl-4-carboxylic acid. The effect on the inicidence of the smectic C phase is quite striking. The butyl to hexyl esters inclusive exhibit this phase, while the heptyl to decyl esters show latent smectic C properties for which "virtual" transition temperatures can be obtained. The temperatures of the S_A to S_C transitions lie on two parabolic curves, the even members lying on the curve representing higher S_C thermal stabilities than those of the odd members. The earlier homologues of the series show S_A, S_B, S_E or S_{AB} properties. The effect on the incidence of the smectic phases was also investigated for molecules containing longer carbon chains. Here the incidence of the smectic C phase is discussed for the methyl to n-nonadecyl esters of 4′-n-octyloxybiphenyl-4-carboxylic acid. This series is roughly divided into three types, with the earlier homologues (methyl to propyl) showing S_A, S_B, S_E or S_{AB} phases, the middle homologues (butyl to octyl) S_A, S_C or S_C "virtual" phases and the later members (nonyl to nonadecyl) only S_A phases.

The effect of branching of a terminal carbon chain is also discussed in relation to the smectic phases and the results are compared with those for a non-branched series. This is done for the 1-methylalkyl esters of 4′-n-octyloxybiphenyl-4-carboxylic acid and the n-alkyl esters of that same acid. The branched series exhibits only S_A and S_C or S_A "virtual" phases, whilst the non-branched series shows S_A, S_{AB}, S_C, S_B or S_E phases.

Finally we investigated the influence of the rigidity or flexibility of the terminal group on the incidence of smectic phases in a range of differently p-substituted-phenyl esters of 4′-n-octyloxybiphenyl-4-carboxylic acid. Particularly interesting is the incidence of the smectic C phase in

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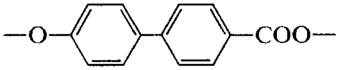
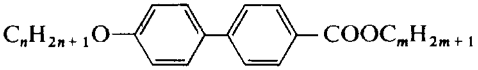
the *p*-alkoxyphenyl esters. All the members (methyl to *n*-decyl) show S_A and S_B phases and the earlier members (methyl to hexyl) exhibit nematic phases as well. As the alkoxy chain is lengthened, the smectic C phase is suddenly injected (from the butyl ester onwards) and the S_B phase is retained, unlike the corresponding *n*-alkyl esters. An attempt was also made to show that a "globular" terminal group in these *p*-substituted phenyl esters does not necessarily mean that the ester will show a S_A, S_B sequence.

INTRODUCTION

In recent work[1], we showed that by just extending a carbon chain in the *n*-alkyl esters of 4′-*n*-heptyloxy, octyloxy and nonyloxy-biphenyl-4-carboxylic acid there was a sudden injection of smectic C properties into these three series of esters. The methyl to *n*-decyl esters of 4′-*n*-hexyloxybiphenyl-4-carboxylic acid, however, only show S_A and S_B properties, and no S_C properties at all. Thus, before a S_C phase is formed, a critical alkoxy chain length and also a critical chain length of the *n*-alkyl ester group must be achieved. Obviously these critical chain lengths are not common to all mesogens and they only relate to the 4′-oxy-biphenyl-4-carboxylate system. Therefore the rest of the mesogen molecule, other than the terminal carbon chains, must play its part too in determining the particular smectic phases obtained. Consequently, this paper is mainly concerned with molecules that have the same "central core" structure, i.e.,



In our recent work,[1] it was found for compounds of structure:



that for $n = 6$; $m = 1$–10, all the esters showed a S_A phase, with the methyl ester showing a S_{AB} transition. Also, all the esters showed a S_B phase, and the methyl to propyl esters had an additional S_E phase.

For $n = 7, 8, 9$; $m = 1$–10, all the esters showed S_A phases except for the methyl ester which showed a S_{AB} transition. All these series of esters were characterised by an injection of S_C properties, usually at a carbon chain length of $m = 4$ (butyl ester), which continued up to a chain length of $n = m$. The S_A–S_C transition temperatures plotted against m gave two smooth, parabolic curves, with the even members (even m) lying on the curve representing higher S_C thermal stabilities. The earlier members of the series ($m = 1$–3) showed S_B or S_B and S_E characteristics underlying the S_A phase.

Thus, this work showed that it is difficult to assign theoretically particular smectic phases even to mesogens with closely related molecular structures, as merely by extending a carbon chain by one carbon we can move from a S_A, S_B sequence to a S_A, S_C sequence.

The present study looks at some wider aspects of changing the molecular architecture whilst always retaining the common core structure referred to above. The effects of extending the carbon chains to extremely long lengths, of branching in the terminal alkyl chains, and of the growth of flexible structures from a terminal phenyl ring are all investigated.

RESULTS

The results presented here are basically concerned with the incidence of the tilted S_C phase in various esters. The results are divided into nine sections.

1 *n*-Alkyl esters of 4'-*n*-decyloxybiphenyl-4-carboxylic acid

Figure 1 represents the results obtained for the methyl to *n*-decyl esters of 4'-*n*-decyloxybiphenyl-4-carboxylic acid. The transition temperature curves are similar to those obtained in previous studies.[1] The transition curves are characterised by the following points:

a) The methyl ester shows a S_{AB}–I transition; the S_B phase is however effectively obtained from the isotropic liquid. All the other esters (ethyl to *n*-decyl) show a S_A phase or a "virtual" S_A phase. The transition temperatures for the S_A to I transition lie on two smooth curves with an alternation of the thermal stabilities between odd and even members. The esters of odd alkyl chain length lie on the curve representing higher thermal stabilities than those of the even members. The last three members (*n*-octyl to *n*-decyl) of the series all have melting points and recrystallisation temperatures above those for the I–S_A transitions. "Virtual" transition temperatures for these three compounds can be obtained by extrapolating the S_A to I transition curves or by miscibility studies with a suitable compound exhibiting a S_A phase.

b) The methyl to propyl esters show S_B phases. The S_B phase observed is uniaxial, and the S_A to S_B transition is not detectable by microscopic observation. The transition bars that characterise most S_A to S_B transitions are not seen, and no clearing in the fan regions is observed. The S_A to S_B transition is however readily detected by means of differential thermal analysis and also by miscibility methods with compounds that show transition bars for the S_A to S_B transition.

c) The methyl and ethyl esters show a biaxial S_E phase; the S_E to S_B transitions lie on a rapidly falling curve, and thus the S_E phase is not observed

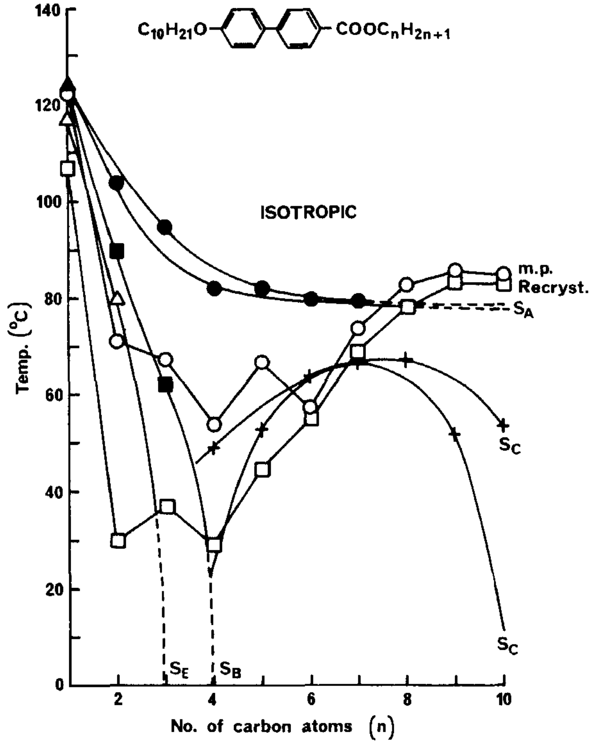


FIGURE 1 Plot of transition temperatures against the number of carbon atoms (*n*) in the *n*-alkyl chain of the esters of 4′-*n*-decyloxybiphenyl-4-carboxylic acid.
Key: ▲, S_{AB}–I; ●, S_A–I; ■, S_B–S_A; △, S_E–S_B; +, S_C–S_A; ○, crystal–S_E, S_C, S_B, S_A or I; □, recrystallisation on cooling. Some transitions are "virtual".

after the ethyl ester. The S_E phase was shown to be biaxial on conoscopic observation.

d) The butyl to hexyl esters exhibit S_C phases, and for the heptyl to decyl esters, S_A–S_C phase transitions can be obtained by miscibility methods, so giving "virtual" phase transition temperatures. The S_C phases of the butyl to hexyl esters gave broken fan and schlieren textures when observed by microscopy. Differential thermal analysis showed no detectable enthalpy peak for the S_A to S_C transition for these three esters. The striking property of the series is unquestionably the sudden injection of S_C character with the transition temperatures for the even members lying on a parabola representing higher thermal stabilities than those of the odd members. The maximum of the parabola is at the octyl ester.

2 *n*-Alkyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid

The results for the methyl to *n*-nonadecyl esters are presented in Figure 2.

The methyl to *n*-decyl esters show virtually the same properties as those for the above series, except for the S_C phase. This phase once again first appears for the butyl ester but only occurs up to the heptyl ester. The interesting point about this series is that it appears to be divided into three regions. The earlier members (methyl to propyl) show S_{AB}, S_A, S_B, S_E phases. Then when the carbon chain is extended to four, there is a switch to a S_A, S_C or S_C "virtual" sequence of phases. This occurs for the butyl to heptyl esters. The S_C transition temperatures again form two parabolae, the upper curve for the even members having its maximum for thermal stability at the hexyl ester. The final part of the series (octyl to nonadecyl) shows only S_A phases. It should be noted that there is still quite a considerable alternation of the transition temperatures from the odd to the even members even at long chain lengths. For a more detailed account of the behavior of the methyl to decyl esters see Ref. 1.

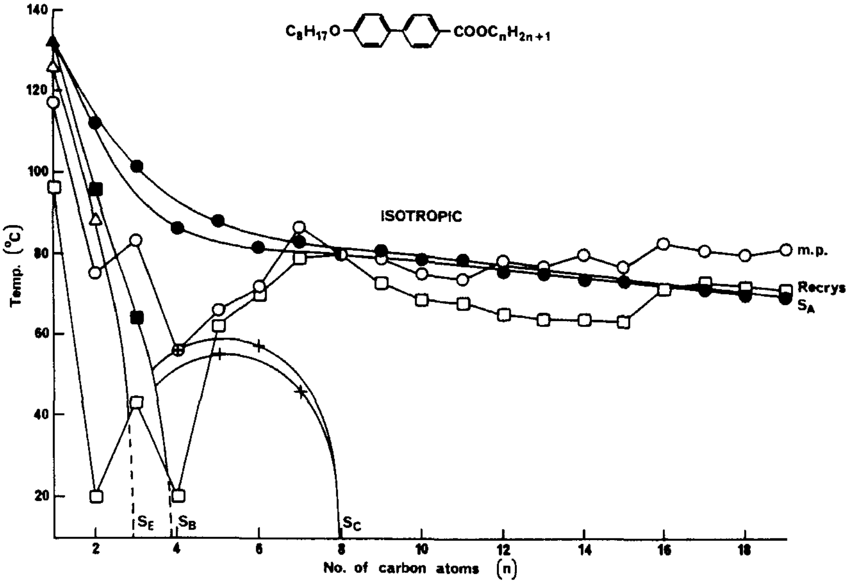


FIGURE 2 Plot of the transition temperatures against the number of carbon atoms (*n*) in the *n*-alkyl chain of the esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid.
Key: ▲, S_{AB}–I; ●, S_A–I; ■, S_B–S_A; △, S_E–S_B; +, S_C–S_A; ○, crystal–S_E, S_A or I; □, recrystallisation on cooling. Some transitions are "virtual".

3 1-Methylalkyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid

The results obtained for this series are shown in Figure 3.

By just making a small change in the structural architecture of the series discussed in Section 2, all the S_B, S_{AB}, and S_E character is lost. The structural change is just a branching of the terminal, ester carbon chain. All the effects of branching the terminal chain are the same as those set out by Gray and Harrison,[2] but here the effect of the branching should be looked at from the standpoint of change in smectic polymorphism. In the "straight" chain series, we have S_{AB}, S_A, S_B, S_E character for the methyl to propyl esters, but for the 1-methylethyl to 1-methylbutyl esters, we have only S_A and S_C character. The S_C transition temperatures of the branched series appear to lie, like those for the non-branched series, on two parabolic curves with an alternation between odd and even members in the same "sense" as that for the "straight" chain series. The curves in the branched series appear however to have been "shunted" along the (*n*) axis, such that only the "tail" ends of the parabolae can be seen.

For the 1-methylpentyl to 1-methyloctyl esters, no S_A, or S_C, phase was observed by microscopy. Therefore, "virtual" transition temperatures were obtained for these esters by extrapolating lines in miscibility diagrams of state. By using the co-miscibility of the S_A phase of the 1-methylalkyl esters and of *n*-butyl 4′-*n*-octyloxybiphenyl-4-carboxylate, the "virtual" transition

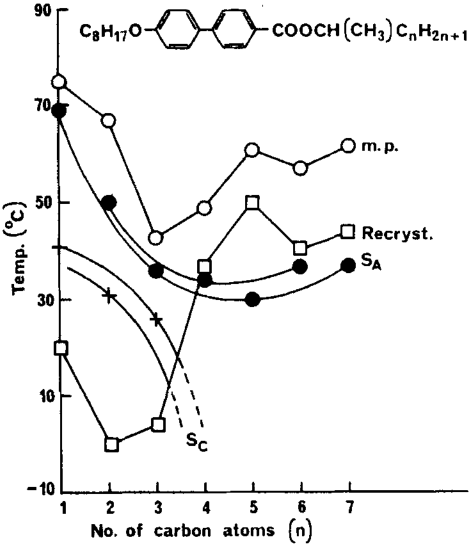


FIGURE 3 Plot of the transition temperatures against the number of carbon atoms (*n*) in the 1-methylalkyl chain of the esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid.
Key: ○, crystal-I; ●, I-S_A; +, S_A-S_C; □, I or S_C-crystal. Some transitions are "virtual".

temperatures for the S_A phases were obtained and also the S_C phase of the *n*-butyl ester was shown to be immiscible with any phase of these four esters. This shows that the S_C transition curve falls sharply away after the 1-methylbutyl ester. The S_C phases of the 1-methylethyl to 1-methylbutyl esters were shown to be miscible with the S_C phase of the *n*-butyl 4′-*n*-octyloxybiphenyl-4-carboxylate.

The S_A to I transition temperatures in the branched series also appear to rise as the series is ascended, unlike those for the non-branched series which level off. However, we cannot be sure of this, as "virtual" transition temperatures obtained by extrapolation are involved.

4 *p*-*n*-Alkoxyphenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid

The results for the methoxy to *n*-decyloxyphenyl esters are contained in Figure 4.

The results can be divided into a number of sections.

a) The methyl to hexyl esters show a nematic phase (Plate 1) which tends to be homeotropic. The nematic to isotropic liquid transition temperatures lie on two smooth curves which approach the S_A to nematic or isotropic liquid transition curves tangentially. The nematic to isotropic liquid transition temperatures show an alternation between the odd and even members, the even members lying on the upper curve.

b) The S_A phase forms mainly as a homeotropic texture with fan regions incorporated in it (Plate 2). The S_A to N or I transition temperatures lie on two smooth curves with the same sense of alternation of thermal stability between the odd and even members as that for the nematic transitions.

c) The S_C to S_A phase transition is suddenly injected for the butyl to decyl esters. Like the *n*-alkyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid, the S_C phase is injected at the butyl ester, but unlike the *n*-alkyl esters, the S_C to S_A phase transition does not fall away at the octyl ester, but continues on up to the decyl ester. The S_C phase, observed microscopically (Plate 5), shows several variations with temperatures. The phase shows schlieren areas that are formed on cooling from homeotropic areas of the S_A phase and broken fan areas that form from fan areas of the S_A phase. The phase shows a marked colour change from blue to yellow to brown on cooling of the schlieren areas, while the fan areas become sandy in appearance and almost indistinguishable from the schlieren areas (Plate 3). Moreover, on cooling the S_C phase about midway through its temperature range, lines are formed in the schlieren areas: these then quickly disappear as the temperature is lowered. The lines in one domain bordered by schlieren "brushes" are at right angles to those in

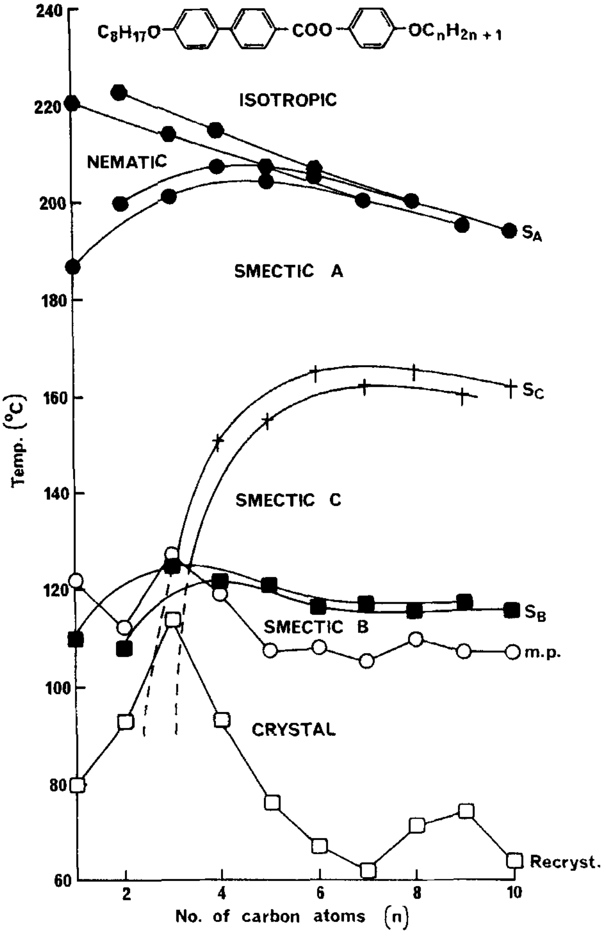


FIGURE 4 Plot of the transition temperatures against the number of carbon atoms (*n*) in the *p*-*n*-alkoxyphenyl group of the esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid.
Key: ●, N–I; ●, S_A–I or N; +, S_C–S_A; ■, S_B–S_A or S_C; ○, crystal–S_A or S_B; □, S_B–crystal.

the next domain—see Plate 6. On further cooling to a temperature just above the S_C to S_B transition, the lines return again, but in a less well defined form.

d) A S_B phase is formed for all the esters; for the methyl to propyl esters, there is a S_A to S_B transition which is characterised again by the lack of transition bars, and the transition is only detected by use of differential thermal analysis. The S_B phase formed from both the S_A and the S_C phases is uniaxial, and the phase shows large homeotropic areas (Plate 4). The S_B phases of the ethyl, hexyl, heptyl, octyl, nonyl and decyl esters were all shown to be unixial by conoscopic observation.

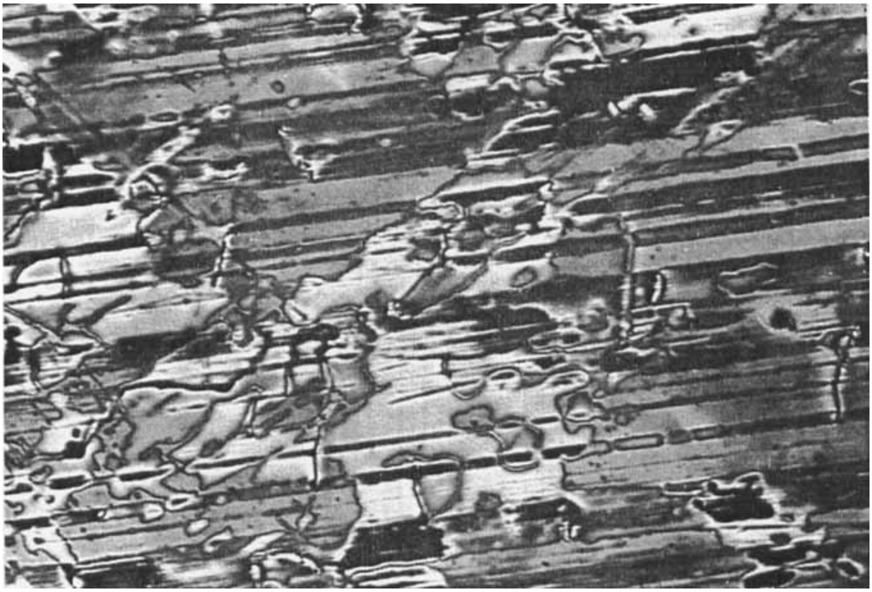


PLATE 1 Texture of the nematic phase of the *p*-*n*-hexyloxyphenyl ester of 4′-*n*-octyloxybiphenyl-4-carboxylic acid showing partially homeotropic and partially homogeneous areas (× 200).

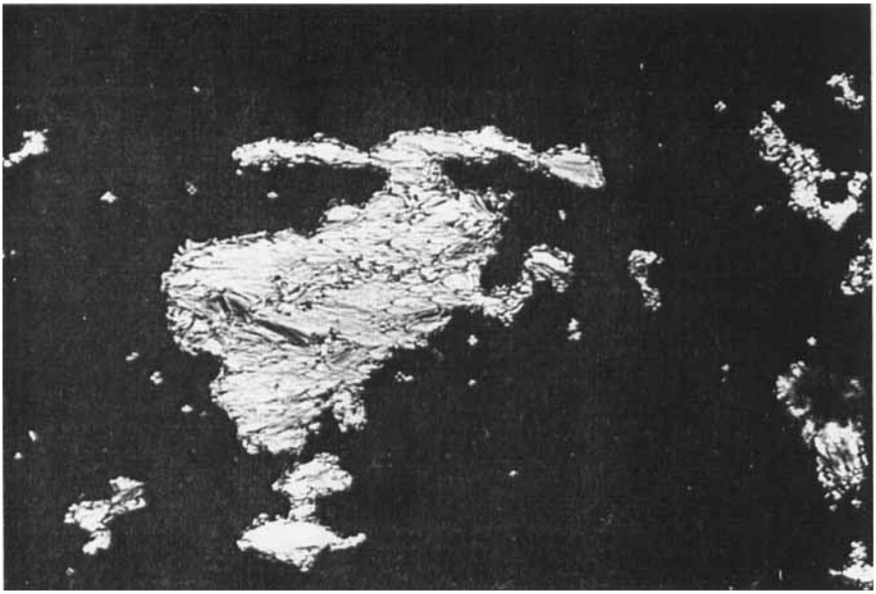


PLATE 2 Fan and homeotropic textures of the S_A phase of the *p*-*n*-hexyloxyphenyl ester of 4-*n*′-octyloxybiphenyl-4-carboxylic acid (× 200). The fan areas are more lined than in the clearer fans obtained with the S_B phase (Plate 4).

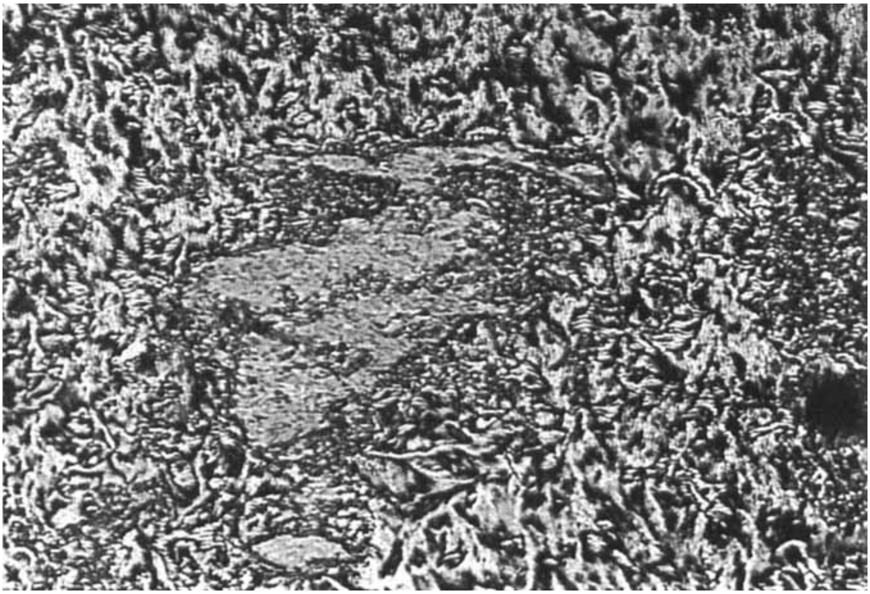


PLATE 3 Broken fan and schlieren textures at lower temperatures in the thermal range of the S_C phase of the *p*-*n*-hexyloxyphenyl ester of 4-*n*′-octyloxybiphenyl-4-carboxylic acid (× 200). The central fan area has become very sandy in appearance and is almost indistinguishable from the now modified schlieren areas.

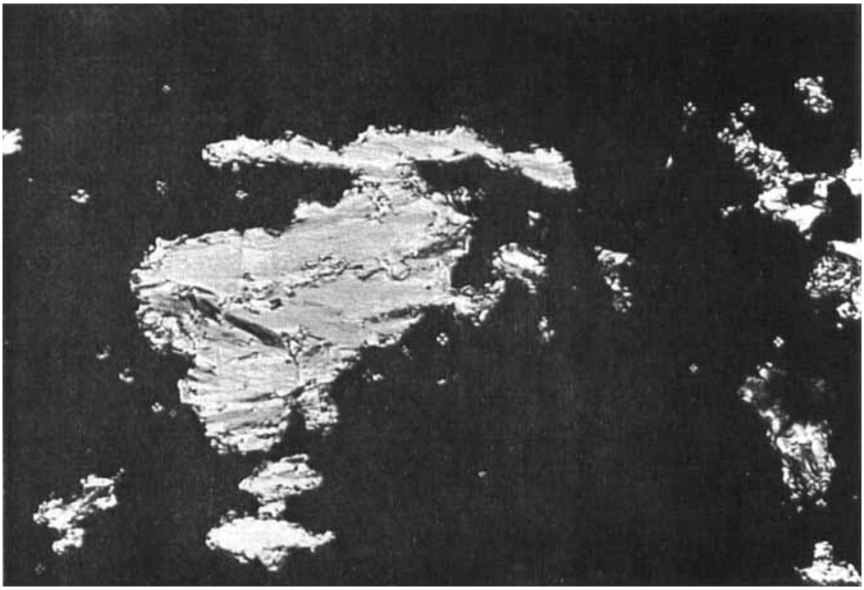


PLATE 4 Fan and homeotropic textures of the S_B phase of the *p*-*n*-hexyloxyphenyl ester of 4′-*n*-octyloxybiphenyl-4-carboxylic acid (× 200). The S_B phase has large homeotropic areas showing that it is uniaxial (confirmed by conoscopic observations). Note the clearer fan areas of the S_B phase compared with those in the same area of the S_A phase (Plate 2).

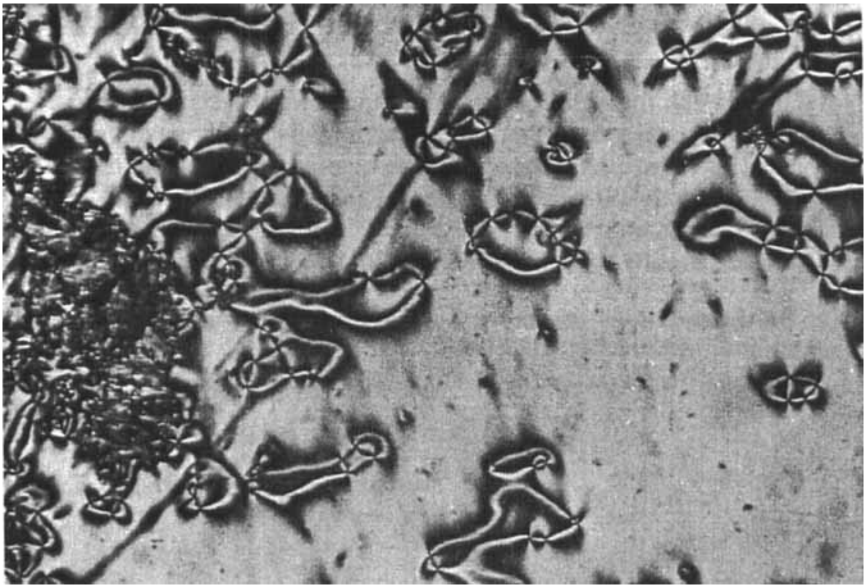


PLATE 5 The schlieren and broken fan textures of the S_C phase of the *p*-*n*-octyloxyphenyl ester of 4′-*n*-octyloxybiphenyl-4-carboxylic acid (× 200).

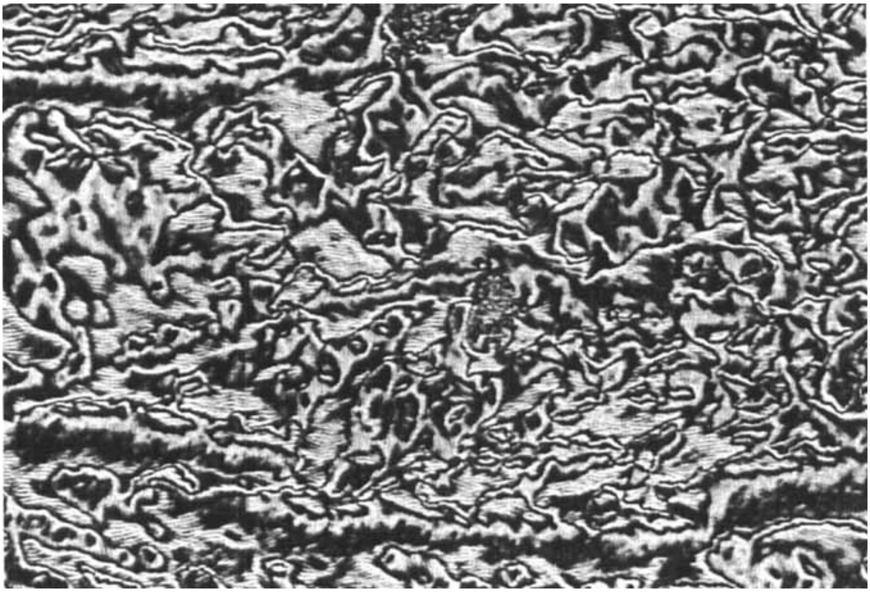


PLATE 6 The lined schlieren texture of the S_C phase of the *p*-*n*-hexyloxyphenyl ester of 4-*n*′-octyloxybiphenyl-4-carboxylic acid (× 200). The lines in the S_C phase come and go at about the mid-point of the thermal range of the phase. The lines in one domain appear to be perpendicular to those in the next domain, the domains being separated by the S_C "brushes".

e) Therefore in this series, there is again a sudden injection of smectic C character, but the smectic B character does not fall off, and remains under the S_C phase. It is important to note that the nematic phase is mainly homeotropic, the S_A phase is markedly homeotropic and uniaxial, the S_C phase is tilted and biaxial, and finally the S_B phase is markedly homeotropic and uniaxial, i.e., an *orthogonal* S_B phase exists under a *tilted* S_C phase.

5 *p*-Halogenophenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid and related Schiff's bases

The results for the two series are presented in Figures 5 and 6.

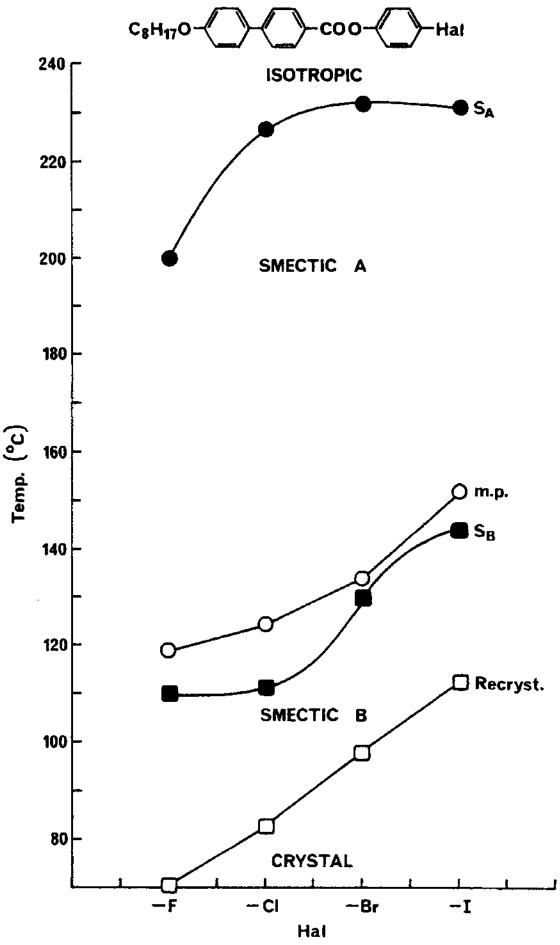


FIGURE 5 Plot of the transition temperatures against the nature of the halogeno-substituent in the *p*-halogenophenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid.
Key: ●, S_A–I; ○, crystal–S_A; ■, S_A–S_B; □, S_B–crystal.

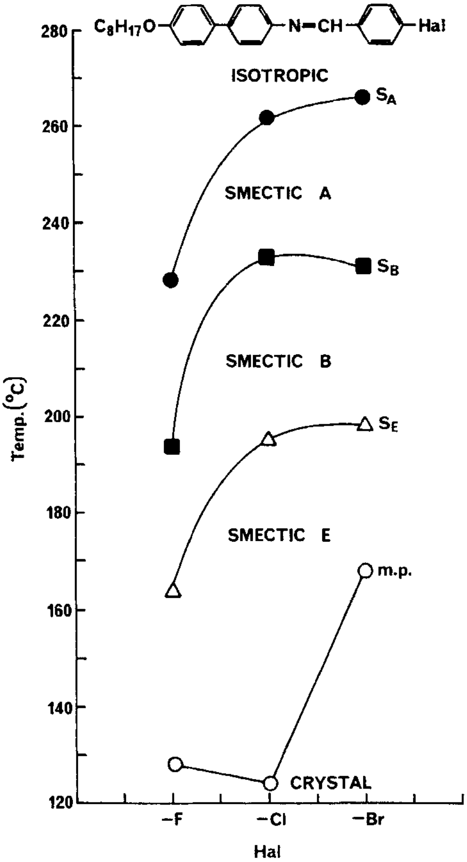


FIGURE 6 Plot of the transition temperatures against the nature of the halogeno-substituent in the *p*-halogenobenzylidene-4′-(4″-*n*-octyloxyphenyl)anilines.
Key: ●, S_A–I; ■, S_B–S_A; △, S_E–S_B; ○, crystal–S_E.

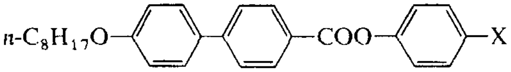
It is better to consider the results for these compounds together, rather than separately.

a) Starting with the fluoro compound, both series show a rise in S_A thermal stability which levels off for the bromide (and iodide).

b) Both series show S_B character, but each has quite differently shaped curves for the transition temperatures. The esters show a sudden increase in transition temperature from the chloride to the bromide, whereas the Schiff's bases show a maximum at the chloride and a falling-off in transition temperature for the bromide.

c) The Schiff's bases show enantiotropic S_E phases, the curve for the transition temperatures mirroring that for the S_A–I phase transitions. The esters show *no* S_E phase at all.

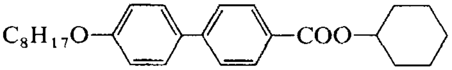
6 Various *p*-substituted-phenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid



These compounds have not had their transition temperatures plotted graphically but a list of sequences of phase transitions is given below.

X	Phase Sequence
—H	S_B, S_A
—CHO	S_B, S_A, N
—COCH$_3$	S_B, S_A
—COOCH$_3$	S_B, S_A
—COOC$_2$H$_5$	S_B, S_A
—C$_3$H$_7$-*n*	S_B, S_A
—C(CH$_3$)$_3$	S_C, S_A

Also prepared was:



which showed a S_A, S_C sequence.

In previous work,[1,3] a similar situation was studied for the analogous Schiff's bases. It was suggested from the results that if the terminal group X was of a globular nature, then a S_A, S_B, S_E phase sequence would be obtained. From the above results, however, it would appear that for one globular group, i.e., —C(CH$_3$)$_3$, this reasoning is not applicable to esters, as a S_A, S_C phase sequence is obtained for the *p*-*t*-butylphenyl ester.

7 Miscibility studies

A large number of miscibility diagrams of state for mixtures of the various esters with one another and with certain standard materials exhibiting known smectic phases was obtained. The main features are summarised below.

n-Butyl 4′-*n*-octyloxybiphenyl-4-carboxylate was shown to be miscible with 4-*n*-octyloxybenzoic acid which is a standard compound showing N and S_C phases—see Figure 7. The now standard S_C ester, *n*-butyl 4′-*n*-octyloxybiphenyl-4-carboxylate was used to show that the butyl to hexyl esters of 4′-*n*-decyloxybiphenyl-4-carboxylic acid posses S_C and S_A phases (Figure 8). The same compound was also used to find "virtual" S_A to S_C transitions for the heptyl to decyl esters of 4′-*n*-decyloxybiphenyl-4-carboxylic acid. The

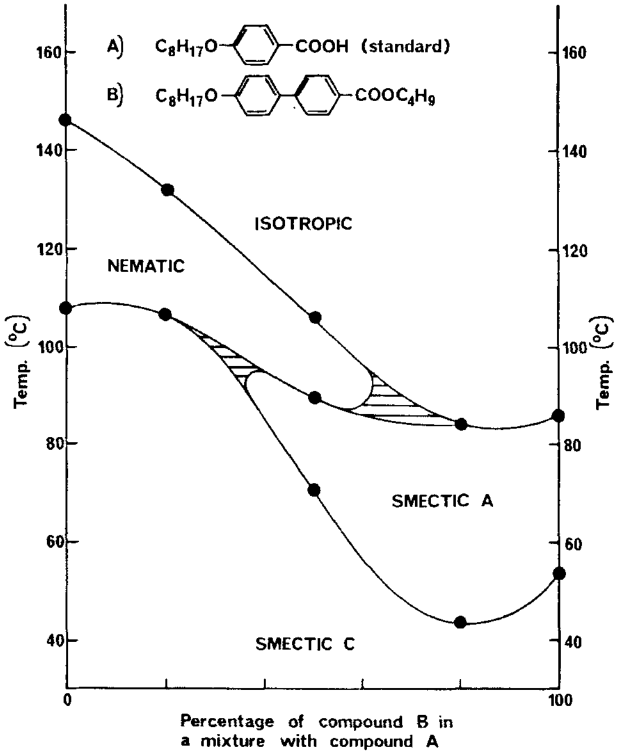


FIGURE 7 Diagram of state of mixtures (wt. %) of 4-*n*-octyloxybenzoic acid (A) with *n*-butyl 4′-*n*-octyloxybiphenyl-4-carboxylate (B).

transition temperatures for the methyl to *n*-decyl esters of the decyloxy series are to be found in Table I.

The branched 1-methylalkyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid were also shown to have S_A and S_C phases by co-miscibility with the phases of the same standard S_A, S_C ester above. The seven members of the series were all shown to have S_A or latent S_A phases, whilst only the first three members had S_C properties.

Finally, the *p*-*n*-alkoxyphenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid were shown to have S_A and S_B phases for the methoxy to propyloxy members by their co-miscibility with *n*-decyl 4-(*p*-phenylbenzylideneamino)cinnamate (Figure 9). The butyloxy to decyloxy esters were shown to have a S_C phase by their co-miscibility with the standard ester *n*-butyl 4′-*n*-octyloxybiphenyl-4-carboxylate.

Other "virtual" transition temperatures and transition temperatures for all the compounds in the six series can be found in Tables I to VI inclusive.

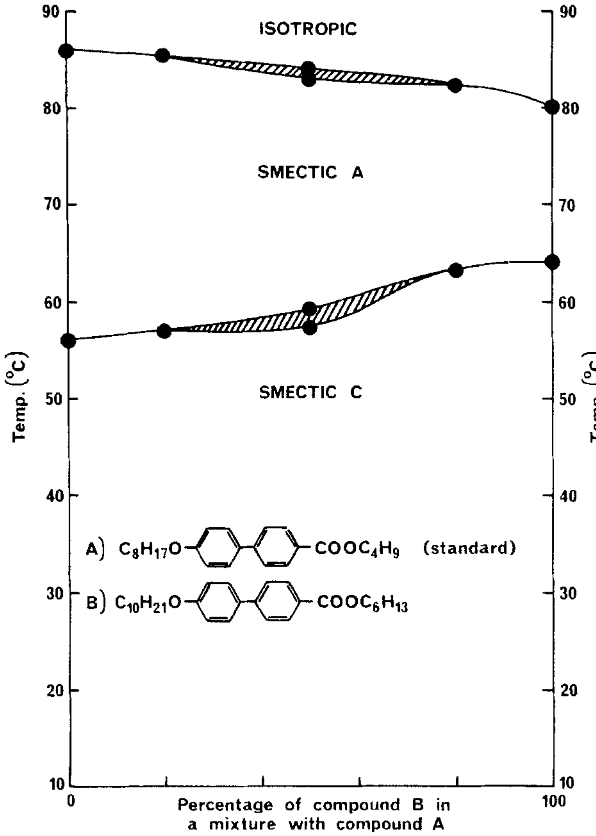
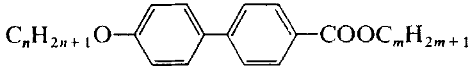


FIGURE 8 Diagram of state for mixtures (wt. %) of *n*-butyl 4′-octyloxybiphenyl-4-carboxylate (A) with *n*-hexyl 4′-*n*-decyloxybiphenyl-4-carboxylate (B).

8 Differential thermal analysis

From differential thermal analysis, enthalpy values for transitions involving the smectic C phases were obtained only for the following compounds.



n	*m*	ΔH, C-S_C	ΔH, S_C-S_A	ΔH, S_A-I
7	4	1.95	0.5	1.62
8	4	1.36	0.24	1.2
9	4	6.04	0.48	1.69

Values in kcal mol^{-1}

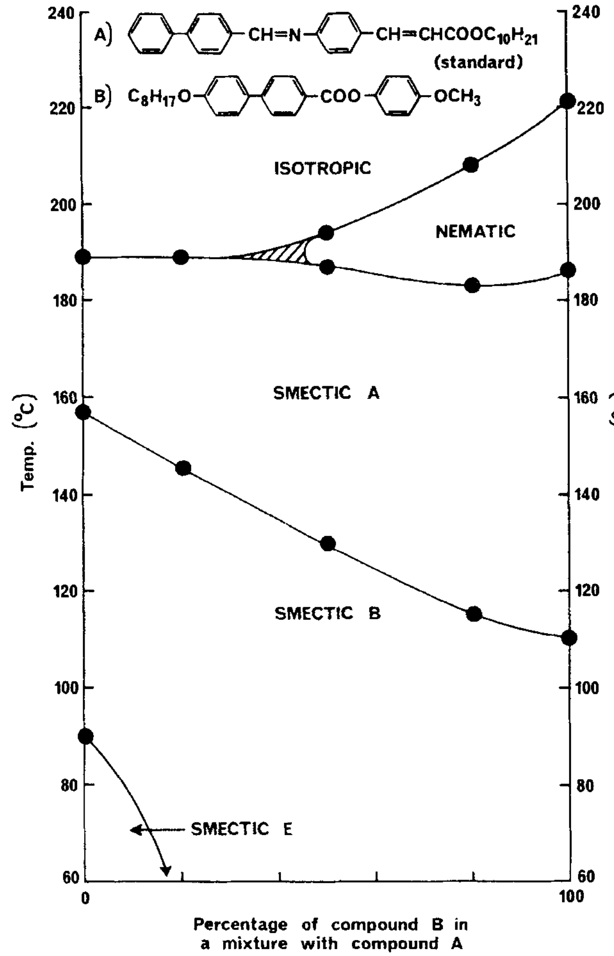
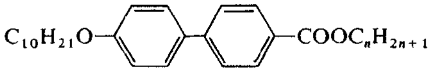


FIGURE 9 Diagram of state for mixtures (wt. %) of *n*-decyl 4-(-*p*-phenylbenzylideneamino)-cinnamate (A) with the *p*-methoxyphenyl ester of 4′-*n*-octyloxybiphenyl-4-carboxylic acid (B).

Values for the enthalpies could not be obtained for the S_C phase of the *n*-alkyl 4′-*n*-decyloxybiphenyl-4-carboxylates or the 1-methylalkyl 4′-*n*-octyloxybiphenyl-4-carboxylates or even the *p*-*n*-alkoxyphenyl 4′-*n*-octyloxybiphenyl-4-carboxylates. The S_C peaks could hardly be detected by differential thermal analysis at a normal sensitivity, and for some compounds, no peaks were registered at all. It is however interesting to note that for the butyl to hexyl esters of 4′-*n*-decyloxybiphenyl-4-carboxylic acid, the size of the very small peaks decreased from the butyl to the hexyl ester.

TABLE I

Transition temperatures in °C for the compounds of structure

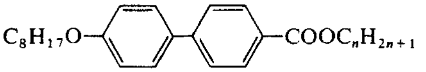


n in C_nH_{2n+1}	$C \rightarrow S$ or I	$S_E \rightarrow S_B$	$S_B \rightarrow S_A$	$S_C \rightarrow S_A$	$S_A \rightarrow I$	Recryst. temp.
1	122	(117)	—	—	124[b]	107
2	71	80	90	—	104	30
3	68	—	(62)	—	95	37
4	54	—	—	(49)	82	30
5	66	—	—	(53)	82	45
6	58	—	—	(64)	80	55
7	74	—	—	(66)[a]	80	69
8	83	—	—	(67)[a]	78	78
9	86	—	—	(52)[a]	—[c]	83
10	85	—	—	(54)[a]	—[c]	83

( ) Monotropic transition.
[a] "Virtual" transition temperature.
[b] S_{AB}–I.
[c] "Virtual" transition temperatures to be determined.

TABLE II

Transition temperatures in °C for the compounds of structure

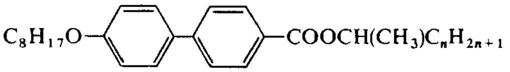


n in C_nH_{2n+1}	$C \rightarrow S$ or I	$S_E \rightarrow S_B$	$S_B \rightarrow S_A$	$S_C \rightarrow S_A$	$S_A \rightarrow I$	Recryst. temp.
1	117	126	—	—	132[b]	96
2	75	88	96	—	112	20
3	83	—	(64)	—	101	43
4	56	—	—	(56)	86	20
5	66	—	—	(55)[a]	88	62
6	72	—	—	(56)[a]	82	70
7	87	—	—	(46)[a]	(83)	79
8	80	—	—	—	(80)	80
9	79	—	—	—	80	73
10	75	—	—	—	79	69
11	74	—	—	—	79	68
12	78	—	—	—	(76)	65
13	77	—	—	—	(76)	64
14	80	—	—	—	(74)	64
15	77	—	—	—	(74)	63
16	83	—	—	—	(72)	72
17	81	—	—	—	(72)[a]	73
18	80	—	—	—	(70)[a]	72
19	81	—	—	—	(69)[a]	71

( ) Montropic transition.
[a] "Virtual" transition temperature.
[b] S_{AB}–I.

TABLE III

Transition temperatures in °C for the compounds of structure



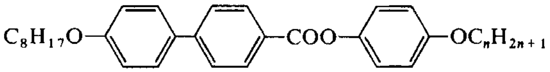
n in C_nH_{2n+1}	C → S or I	$S_C \to S_A$	$S_A \to I$	Recryst. temp.
1	75	(41)	(69)	20
2	67	(31)	(50)	0
3	43	(26)	(36)	4
4	49	—	(34)[a]	37
5	61	—	(30)[a]	50
6	57	—	(37)[a]	41
7	61	—	(37)[a]	44

( ) Monotropic transition.

[a] "Virtual" transition temperature.

TABLE IV

Transition temperatures in °C for the compounds of structure

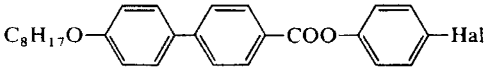


n in C_nH_{2n+1}	C → S or I	$S_B \to S_A$ or S_C	$S_C \to S_A$	$S_A \to$ N or I	N → I	Recryst. temp.
1	122	(110)	—	187	221	80
2	112	(108)	—	200	223	93
3	127	(125)	—	201	214	114
4	119	122	150	207	215	93
5	107	121	155	204	207	76
6	108	116	165	205	207	67
7	105	117	162	200	—	62
8	110	116	165	200	—	71
9	107	117	160	195	—	74
10	107	116	162	194	—	64

( ) Monotropic transition.

TABLE V

Transition temperatures in °C for the compounds of structure

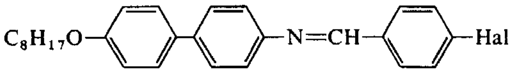


Hal	$C \to S_A$	$S_B \to S_A$	$S_A \to I$	Recryst. temp.
F	119	(110)	200	70
Cl	124	(111)	226	83
Br	134	(130)	232	98
I	152	(144)	231	112

( ) Monotropic transition.

TABLE VI

Transition temperatures in °C for the compounds of structure

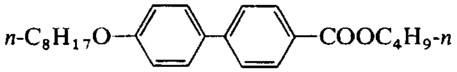


Hal	C → S_E	S_E → S_B	S_B → S_A	S_A → I
F	128	164	194	228
Cl	124	195	233	262
Br	168	198	231	266

9 X-ray diffraction analysis

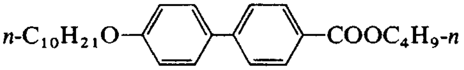
The lamellar spacings for certain of the compounds that exhibit S_C phases have been obtained by X-ray diffraction.

a)



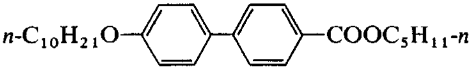
Temp. (°C)	Spacing (Å)	Expected phase
80	26.6 ± 0.4	S_A
70	26.6 ± 0.4	S_A
60	26.6 ± 0.4	S_A
54	27.0 ± 0.4	S_C
45	26.8 ± 0.4	S_C
35	26.8 ± 0.4 25.4 ± 0.4	S_C to crystal

b)



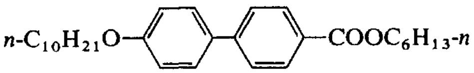
Temp. (°C)	Spacing (Å)	Expected phase
60	24.9 ± 0.35	S_A
40	24.8 ± 0.35	S_C
23	24.9 ± 0.35	Crystal

c)



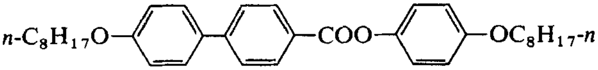
Temp. (°C)	Spacing (Å)	Expected phase
75	26.7 ± 0.4	S_A
60	26.7 ± 0.4	S_A
50	26.3 ± 0.4	S_C
23	26.3 ± 0.4	Crystal

d)



Temp. (°C)	Spacing (Å)	Expected phase
75	28.1 ± 0.4	S_A
68	28.5 ± 0.4	S_A
62	28.25 ± 0.4	S_C
50	28.25 ± 0.4	Crystal
22	28.15 ± 0.4	Crystal

e)

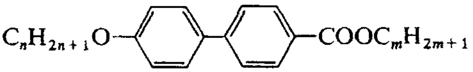


Temp. (°C)	Spacing (Å)	Expected phase
178	36.6 ± 0.4	S_A
173	36.6 ± 0.4	S_A
170	36.6 ± 0.4	S_A
166	36.6 ± 0.4	S_A
164	36.1 ± 0.4	S_A
163	36.1 ± 0.4	S_C
153	35.2 ± 0.4	S_C
143	34.3 ± 0.4	S_C
133	34.3 ± 0.4	S_C
128	33.9 ± 0.4	S_C
120	33.9 ± 0.4	S_C
117	33.9 ± 0.4	S_C
115	38.0 ± 0.5	S_B
110	38.0 ± 0.5	S_B
23	33.8 ± 0.4	Crystal

DISCUSSION

The discussion can be split into several parts, all relating to molecules with the same "central" core.

1 The effect of extending a *n*-alkyl chain for compounds of structure



For $n = 6$; $m = 1$–10, only S_A and S_B phases are observed across the series. When $n = 7$, then the first S_C phase is observed in these *n*-alkyl esters, and this occurs only for a value of $m = 4$. However, "virtual" S_A to S_C transitions are obtained up to $m = 7$. For $n = 8$, we have exactly the same behavior, and for $n = 9$, again at a value of $m = 4$, a S_C phase is observed. However, this time the "virtual" S_A to S_C transitions occur up to $m = 8$. Finally, for $m = 10$, S_C phases are observed for $m = 4$, 5, and 6 and "virtual" S_A to S_C transitions are obtained for $m = 7$, 8, 9, and 10.

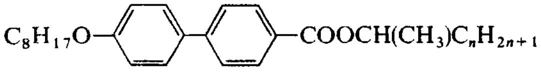
It is interesting also to note the value of m for the maximum of the upper parabola for each series: $n = 7, m = 6$; $n = 8, m = 6$; $n = 9, m = 6$; $n = 10, m = 8$.

Thus it appears that the most thermally stable smectic C phase in each series occurs at a value of $m \sim n - 2$ for $n > 6$. McMillan's theory[4] of the smectic C phase states that one of the factors favouring the smectic C phase relative to the smectic A phase is an approximate molecular centre of symmetry. Certainly this does not appear to be true for the above compounds, and with respect to the alkyl chain lengths, the most thermally stable smectic C is not at equal chain lengths, i.e., $m = n$ but is somewhat off-set towards a slightly more unsymmetrical molecule, i.e., at $m = n - 2$. Thus the most thermally stable smectic C phase occurs in compounds which are not quite symmetrical.

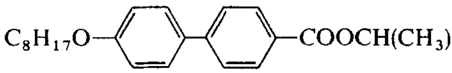
Also of interest are the X-ray analysis figures for the S_A and S_C phases for $n = 8$; $m = 4$ and $n = 10$; $m = 4$, 5, and 6. These experimental values for the lamellar spacings are shorter than the overall molecular lengths. It is important also to note that there is no real change in lamellar spacing on passing from the S_A phase to the S_C phase, and if this is linked with the fact that the enthalpies for the S_A to S_C transitions are either very small or effectively unmeasurable in some cases, it would appear that there is little structural difference between S_A and S_C phases. Recently[5,6] it has been suggested that for at least some S_A phases the molecules oscillate about a central point with a gyroscopic motion. If we now consider the present results in the light of this possibility, then the absence of any real change in lamellar spacing at the S_A to S_C transition and also of any real change in energy at this transition, could be associated with an easy change of one phase to the other by a simple freezing or damping out of the gyroscopic motion. This would fit with the observed lamellar spacings if the tilt angle of the gyroscopic motion in the S_A phase is only 1° or 2° different from the tilt angle of the S_C phase. Thus the transition from a S_A phase to a S_C phase would be easy, since with the cessation of the gyroscopic motion, the molecules would be in a near perfect position for the formation of the S_C phase.

2 The effect of branching at the first carbon of a terminal alkyl chain

For the compounds of structure:



The S_C phase is obtained for $n = 1$ to 3 and the S_A phase is obtained across the entire series examined. Thus, by branching the terminal chain, the occurrence of the S_C phase has been moved to lower values of n than for the n-alkyl esters. Once again this is not in total agreement with McMillan's Theory[4] of the S_C phase. By branching the molecule, we have effectively destroyed any of the symmetry that the n-alkyl esters had, and certainly the most thermally stable S_C phase is formed by the member of the branched series with $n = 1$, i.e., by:

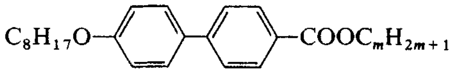


a molecule which does not posses any real "approximate" centre of symmetry as defined by McMillan.

The branching of the terminal chain has destroyed all the S_B and S_E character for the 4′-n-octyloxybiphenyl-4-carboxylate system. Branching in this series thus increases the chance of obtaining the S_C phase in the earlier members and also depresses the S_B and S_E tendencies. The steric model of Wulf[7] considers the S_C phase to be given by molecules having a "zig-zag" type of conformation. However, in this series, by branching the terminal alkyl chain, we are moving away from a "zig-zag" conformation and in fact, the molecule of the most thermally stable S_C compound in this series is more "L"-shaped than "Z"-shaped. This is interesting, for the n-alkyl ester which has the most thermally stable S_C phase ($n = 8$; $m = 6$) has a molecular structure which is definitely "zig-zag" shaped.

3 The effect of long alkyl chains on the properties of the esters

For compounds of structure

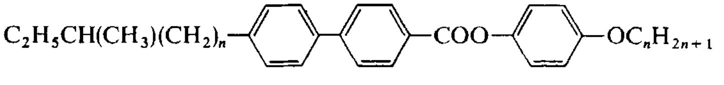


the main observation from the series is that the longer the ester alkyl chain, the more this disfavours the occurrence of any phase underlying the initial phase formed on cooling from the isotropic liquid. For $m = 8$ to 19, only the S_A phase is obtained. It appears therefore that the effect of increase of m up to 8 on the phase sequence is much more critical for each unit increase than when $m = 8$ and over. When the value of $m = 8$ to 19, the S_A to I transition temperature curve becomes level and the melting points and recrystallisation temperatures also become more constant (relative to the fluctuations for the earlier members). Thus it appears that the smectic characteristics of the later members of the series are less dependent than those of the earlier members on the length of the ester alkyl chain. The dividing point between the two extremes is at a value of $m = n$.

4 The *p*-*n*-alkoxyphenyl esters of 4′-*n*-octyloxybiphenyl-4-carboxylic acid

By esterifying 4′-*n*-octyloxybiphenyl-4-carboxylic acid with *p*-*n*-alkoxyphenols, we are changing the basic shape of the central molecular core. In fact we are now looking at the way in which a large, bulky aromatic ring added to a core structure changes the behaviour of that core structure. By adding the phenyl group to the central core, the S_B phase has been stabilised, the S_E phase has been lost, a nematic phase has been added to the earlier members, and the S_C phase has been stabilised particularly in the later members. The S_C phase first appears again at the butyl ester and has a maximum thermal stability at the hexyl ester ($m = n - 2$). The S_C phase thermal stability does not however then fall off rapidly, and S_C phases continue to be observed up to the decyl ester (and probably beyond). These comparisons have been made with respect to the *n*-alkyl esters of the same acid and are a consequence of making the terminal part of the core structure more globular.

It is interesting to compare the results for this series with those obtained by Gray and McDonnell[8] for the esters of structure:



These related esters show only N and S_C properties and possibly latent S_B character as well. This once again shows that branching in terminal chains favours the S_C phase and disfavours the S_B phase, as there is only a possibility that this phase is present.

The tilt angle and enthalpy values for the S_C phase contrast sharply with the results obtained in section 1. The S_C phase does not show a constant tilt angle. Again there is not much change in the lamellar spacing on moving from the S_A to the S_C phase, but there is a large, temperature dependent, change in lamellar spacing (see Figure 10) within the S_C phase. It would also appear from the results so far obtained that there is a metastable tilt position in th S_C phase which corresponds to a temperature of 130–140° in the octyloxyphenyl ester. It is also interesting to note that the lines observed microscopically in the S_C phase occur at around the same temperature. Thus the S_C phase is apparently divided into two regions. On cooling the S_C phase to the end of its phase length, there is a sudden increase in lamellar spacing with the change of phase type from a S_C to a S_B phase. The S_B

lamellar spacing value is greater than the predicted molecular length, indicating very strongly that the S_B phase is orthogonal.

Thus, for these molecules we may have a gyroscopic S_A phase which, on cooling, gives a tilted S_C phase which initially has a tilt angle about the same as the S_A gyroscopic tilt angle; the transition shows no enthalpy peak at all on differential thermal analysis, which is to be expected. The tilt angle then changes with temperature and this probably accounts for the colour changes observed for the phase. The molecules then right themselves on cooling to give an orthogonal S_B phase.

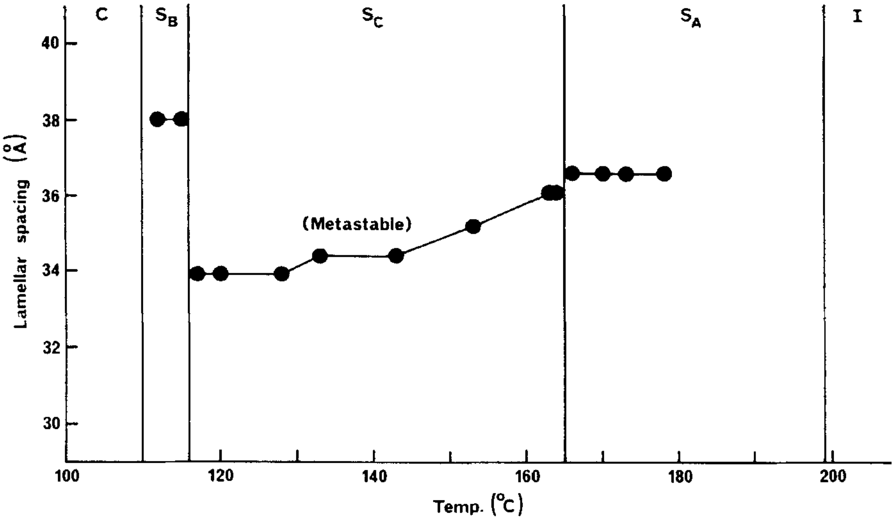
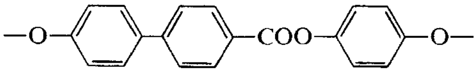


FIGURE 10 Plot of the variation of lamellar spacing in Å against temperature for the *p*-octyloxyphenyl ester of 4′-*n*-octyloxybiphenyl-4-carboxylic acid.

It is possible that the occurrence of more than one stable tilt orientation for the Sc phase is explained by the change in molecular structure, i.e., by making the core more complex:



It would also appear that the more complex the central core structure is, then the greater is the likelihood that the S_C tilt angle will vary with temperature.

5 The *p*-halagenophenyl esters of 4'-*n*-octyloxybiphenyl-4-carboxylic acid and related Schiff's bases

Here we have the same "central core" as that in the previous section, but now an electron rich halogen is attached to it. Consequently, as we do not have two terminal alkyl chains in the compounds, we do not obtain a S_C phase. The nematic phase has also been eliminated, and this may also be connected with the globular shape of the end group and its electron rich nature. A S_A and a S_B phase are obtained once again, showing that the extension of the central core favours the S_B phase.

If these compounds are now compared with the related Schiff's bases, the major difference found is that the Schiff's bases show a S_E phase. It is unlikely that this is explained by a greater ability of the S_B phases of the Schiff's bases to supercool (see Figures 5 and 6), and it would therefore seem that the central —N=CH— linkage favours S_E phases more than the central —COO— linkage. It appears therefore that the occurrence of the S_B phase is determined mainly by the overall shape of the core structure, and is rather insensitive to the particular structural change under consideration within the core. The S_E phase, on the other hand, is very sensitive to this structural change within the core structure, and this, may be because the change affects the ability of the hexagonal net of the S_B phase to contract in one direction in order to form the S_E phase.

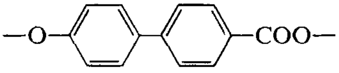
If the transition temperature curves for the S_B phases of the esters and the Schiff's bases are compared, it can be seen that the *p*-chloro derivatives of the two types of compound differ greatly in their transition temperatures relative to those of the other members of the series. That is, the S_A to S_B transition temperature for the *p*-chloro ester is much lower with respect to the other members of the series than is the corresponding transition temperature for the *p*-chloro Schiff's base. Therefore, although the central linkage in the "central core" does not appear to affect the incidence of the S_B phase, it does affect the S_B to S_A transition temperatures and consequently the shapes of the transition temperature curves for the S_B phase.

6 Various *p*-substituted-phenyl esters of 4'-*n*-octyloxybiphenyl-4-carboxylic acid

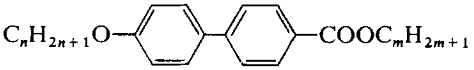
In previous work[1,3] on certain Schiff's bases, it appeared that if a terminal group was of a globular nature and lay along the long axis, e.g., CH_3, Hal, then a S_A, S_B sequence of phases was obtained, and if the terminal group was non-globular and deviated from colinearity with the major axis, then a S_A, S_C sequence was obtained. In this present study we have looked at a more varied group of compounds involving terminal groups that ranged from heavy and rigid at one extreme to flexible at the other. However, within the series of compounds, the nature of the substituent changed only slightly on passing from one compound to another. The first point to make is that the *p*-*t*-butylphenyl ester with a globular substituent does not show a S_A, S_B sequence, but a S_A, S_C sequence. In this series, therefore, the S_A, S_B tendency does not hold for all globular substituents. However, all the other compounds in the group showed S_A, S_B sequences, no matter whether they contained rigid or flexible terminal groups. Thus it can be concluded that the Schiff's bases strongly prefer to show S_C and S_E properties, whereas esters prefer to show S_B properties. It is also possible that the globular shape of a terminal group will only lead to a S_A, S_B sequence if the globular group is a point mass, e.g., a halogen, and that the terminal *t*-butyl group does not conform to this requirement. The effect of a *p*-*t*-butyl group in the Schiff's base system was not established in the earlier study.

CONCLUSIONS AND SUMMARY

The following conclusions relate solely to the compounds with a "central core" structure:



1) For compounds of structure



When $n = 7$ to 10 and $m = 4$ to $m = n$, we have a smectic C phase injected into the series. The maximum S_C thermal stability occurs at $m \sim n - 2$. It appears therefore that the lengths of the alkyl chains in the compound are critical in relation to whether a S_C phase is formed or not. Thus the S_C phase is dependent on the compound containing two alkyl chains of similar length.

2) Branching in a terminal alkyl chain favours the S_C phase and disfavours S_E and S_B phases with respect to the non-branched analogues.

3) Long alkyl chains do not favour the more ordered smectic phases, e.g., S_B, S_E and S_C, but tend to favour the first formed phase in the series, i.e., S_A.

4) When the central core is made larger or more complex, this favours S_B and S_C phases and also the nematic phase, at short terminal chain lengths.

5) For globular substituents a S_A, S_B sequence, and sometimes a S_E phase is formed with certainty only when the substituent is a point mass, e.g., a a halogeno-substituent.

6) If the possible "gyroscopic motion" in a S_A phase does predetermine the formation of a tilted S_C phase on cooling, cf., the alkyl 4′-*n*-decyloxybiphenyl-4-carboxylates, then the nature of the smectic phase (S_B, S_E, S_C) underlying a S_A phase will be greatly dependent on the structure and degree of molecular motion within that S_A phase.

7) Tilted S_C phases can be succeeded on cooling by either orthogonal or tilted S_B phases.

8) It appears that if the "central core" of a molecule is relatively "simple," then if a S_C phase is formed, there is a greater chance of the S_C phase having a constant tilt angle. If however, the "central core" is of a more "complex" nature, then the greater is the chance of obtaining a S_C phase which has a tilt angle that varies with temperature.

9) If the S_C tilt angle varies with temperature, then it is likely that the phase observed microscopically will show colour changes with temperature. Microscopic lines may arise in the schlieren areas, separating different "metastable" tilt positions for the S_C phase.

EXPERIMENTAL

Preparation of materials

All the esters were made by fairly standard procedures. Two main methods were used for the esterifications:

1) *Sulphuric acid method*

a) This method was used for the preparation of the methyl to *n*-butyl esters and also the branched chain esters. The method is therefore for shorter chain esters. The acid (1 g) was dissolved in an excess of the alcohol (15–30 ml) and to the solution, concentrated sulphuric acid (0.6 ml) was added. The mixture was heated under reflux for 5 hr. The hot reaction mixture was then poured into an excess of saturated sodium hydrogen carbonate solution (500–600 ml, depending on the solubility of the alcohol). The precipitated solid was then filtered off and recrystallised from petroleum-ether (b.p. 40–60°); the hot solution was filtered to remove any acid impurities.

b) For esterifications using alcohols of longer chain length, i.e., *n*-pentyl up to *n*-decyl, the above method was adapted as follows: The acid (1 g) was dissolved in an excess of the alcohol (10–15 ml) and to the mixture was added benzene (30 ml) and concentrated sulphuric acid (0.6 ml). The mixture was heated under reflux for 5 hr, then the cooled reaction mixture was washed with saturated sodium hydrogen carbonate solution (2 × 50 ml) and water (1 × 50 ml), and dried over anhydrous sodium sulphate. The benzene solution was filtered and evaporated down until only the solution of the product in the alcohol remained. To this solution petroleum-ether (b.p. 40–60°, 15 ml) was added and the well mixed solution was chilled in a refrigerator overnight. The resulting precipitate was filtered off and recrystallised from petroleum-ether (b.p. 40–60°), the hot solution again being filtered to remove any acid impurities.

2) *Acid Chloride method* This method was used for esterification involving long chain alcohols (*n*-undecyl to *n*-nonadecyl) and also phenols. To the carboxylic acid (0.0015 mol), an excess of thionyl chloride (20 ml) was added and the mixture was heated under reflux on a boiling water bath for 2–3 hr. The hot solution was then evaporated to dryness and the resulting solid acid chloride was dissolved in dry pyridine (20 ml). This solution was cooled in ice and stirred. To this, a solution of the alcohol or phenol (0.0018 mol) in benzene (18 ml) was added. The mixture was allowed to stir for a further 18 hr, being gradually allowed to come to room temperature as the ice melted. It was then heated on a water bath for a further hour. The benzene–pyridine solution was evaporated to dryness. The residue was taken up in a small amount of chloroform (10 ml) and then the solution was run down a silica gel column (2 × 60 cm) using chloroform as eluant. The ester was eluted first. It was then isolated and recrystallised from petroleum-ether (b.p. 40–60°).

The purities of all the resulting esters were established by infra-red spectroscopy, mass spectrometry, thin layer chromatography and elemental analysis. The results for the elemental analysis are given in tables at the end of the paper.

3) *Physical measurements* Observations of microscopic textures and measurements of transition temperatures for all the esters, and also the miscibility studies with certain other compounds were carried out using a Nikon polarising microscope in conjunction with a Mettler FP 52 heated stage and control unit. Checks on transition temperatures, the detection of the S_A to S_B transition for certain of the compounds, and the measurement of enthalpies of transition were made using a Stanton–Redcroft low temperature differential thermal analyser—model 671 B.

Elemental Analysis Figures for Compounds of Structure
$C_nH_{2n+1}OC_6H_4C_6H_4COOC_mH_{2m+1}$

			% Required			% Found	
n	m	M.W.	%C	%H	%O	%C	%H
6	1	312	76.9	7.7	15.4	77.1	7.9
	2	326	77.3	8.0	14.7	77.2	8.1
	3	340	77.6	8.2	14.2	77.7	8.2
	4	354	78.0	8.5	13.5	77.9	8.5
	5	368	78.3	8.7	13.0	78.4	8.7
	6	382	78.5	8.9	12.6	78.4	9.0
	7	396	78.8	9.1	12.1	78.9	9.3
	8	410	79.0	9.3	11.7	79.1	9.3
	9	424	79.3	9.4	11.3	79.3	9.5
	10	438	79.5	9.6	10.9	79.5	9.6
7	1	326	77.3	8.0	14.7	77.3	8.1
	2	340	77.6	8.2	14.2	77.5	8.3
	3	354	78.0	8.5	13.5	78.0	8.4
	4	368	78.3	8.7	13.0	78.4	8.7
	5	382	78.5	8.9	12.6	78.5	9.0
	6	396	78.8	9.1	12.1	78.7	9.2
	7	410	79.0	9.3	11.7	79.0	9.4
	8	424	79.3	9.4	11.3	79.1	9.5
	9	438	79.5	9.6	10.9	79.3	9.8
	10	452	79.7	9.7	10.6	79.9	9.7
9	1	354	77.9	8.5	13.6	78.0	8.5
	2	368	78.2	8.7	13.1	78.3	8.7
	3	382	78.5	8.9	12.6	78.5	8.9
	4	396	78.8	9.1	12.1	79.0	9.3
	5	410	79.0	9.3	11.7	79.2	9.3
	6	424	79.2	9.4	11.4	79.2	9.5
	7	438	79.5	9.6	10.9	79.4	9.7
	8	452	79.6	9.7	10.7	79.4	9.7
	9	466	79.8	9.9	10.3	79.6	9.9
	10	480	80.0	10.0	10.0	80.0	10.1
10	1	368	78.2	8.7	13.1	78.4	8.7
	2	382	78.5	8.9	12.6	78.4	8.9
	3	396	78.8	9.1	12.1	78.8	9.2
	4	410	79.0	9.3	11.7	78.9	9.3
	5	424	79.2	9.4	11.4	79.2	9.6
	6	438	79.5	9.6	10.9	79.7	9.8
	7	452	79.6	9.7	10.7	79.4	9.9
	8	466	79.8	9.9	10.3	79.6	10.0
	9	480	80.0	10.0	10.0	80.2	10.1
	10	494	80.2	10.1	9.7	80.3	10.2

Elemental Analysis Figures for Compounds of Structure
$C_nH_{2n+1}OC_6H_4C_6H_4COOC_mH_{2m+1}$

			% Required			% Found	
n	*m*	M.W.	%C	%H	%O	%C	%H
8	1	340	77.6	8.2	14.2	77.5	8.0
	2	354	77.9	8.5	13.6	78.1	8.4
	3	368	78.2	8.7	13.1	78.3	8.7
	4	382	78.5	8.9	12.6	78.4	9.0
	5	396	78.8	9.1	12.1	78.9	9.2
	6	410	79.0	9.3	11.7	78.8	9.0
	7	424	79.2	9.4	11.4	79.3	9.5
	8	438	79.5	9.6	10.9	79.5	9.6
	9	452	79.6	9.7	10.7	79.8	9.7
	10	466	79.8	9.9	10.3	79.9	9.9
	11	480	80.0	10.0	10.0	79.8	10.1
	12	494	80.2	10.1	9.7	80.1	10.2
	13	508	80.3	10.2	9.5	80.4	10.5
	14	522	80.6	10.3	9.1	80.7	10.5
	15	536	80.6	10.4	9.0	80.4	10.5
	16	550	80.7	10.5	8.8	80.8	10.6
	17	564	80.9	10.6	8.5	80.7	10.7
	18	578	81.0	10.7	8.3	81.1	10.8
	19	592	81.1	10.8	8.1	80.9	10.7

Elemental Analysis Figures for Compounds of Structure
$C_8H_{17}OC_6H_4C_6H_4COOCH(CH_3)C_nH_{2n+1}$

		% Required			% Found	
n	M.W.	%C	%H	%O	%C	%H
1	368	78.2	8.7	13.1	78.1	8.7
2	382	78.5	8.9	12.6	78.6	9.0
3	396	78.8	9.1	12.1	78.6	9.1
4	410	79.0	9.3	11.7	79.1	9.2
5	424	79.2	9.4	11.4	79.4	9.6
6	438	79.5	9.6	10.9	79.4	9.7
7	452	79.6	9.7	10.7	79.5	9.9

Elemental Analysis Figures for Compounds of Structure $C_8H_{17}OC_6H_4C_6H_4COOC_6H_4OC_nH_{2n+1}$

		% Required			% Found	
n	M.W.	%C	%H	%O	%C	%H
1	432	77.8	7.4	14.8	77.7	7.5
2	446	78.0	7.7	14.3	78.1	7.8
3	460	78.3	7.8	13.9	78.2	7.8
4	474	78.5	8.0	13.5	78.4	8.2
5	488	78.7	8.2	13.1	78.6	8.2
6	502	78.9	8.4	12.7	78.9	8.3
7	516	79.1	8.5	12.4	79.0	8.6
8	530	79.2	8.7	12.1	79.3	8.8
9	544	79.4	8.8	11.8	79.5	8.9
10	558	79.6	8.9	11.5	79.7	9.0

Elemental Analysis Figures for Compounds of Structure $C_8H_{17}OC_6H_4C_6H_4COOC_6H_4Hal$

		% Required				% Found	
Hal	M.W.	%C	%H	%O	%Hal	%C	%H
F	420	77.1	6.9	11.4	4.6	76.9	7.0
Cl	436.5	74.2	6.6	11.0	8.2	74.5	6.7
Br	481	67.3	6.0	10.0	16.7	67.4	6.0
I	528	61.4	5.5	9.1	24.0	61.6	5.6

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