SMECTIC F TRENDS IN THE 4-(2’-METHYLBUTYL)PHENYL ESTERS OF 4’-n-ALKOXYBIPHENYL-4-CARBOXYLIC ACIDS AND 4’-n-ALKYLBIPHENYL-4-CARBOXYLIC ACIDS

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SMECTIC F TRENDS IN THE 4-(2'-METHYLBUTYL)PHENYL ESTERS OF
4'-n-ALKOXYBIPHENYL-4-CARBOXYLIC ACIDS AND
4'-n-ALKYLBIPHENYL-4-CARBOXYLIC ACIDS (*)

J. W. GOODBY and G. W. GRAY
Department of Chemistry, University of Hull, Hull, HU6 7RX, England

Abstract. — A number of 4-(2'-methylbutyl)phenyl esters of 4'-n-alkyl- and 4'-n-alkoxy-biphenyl-4-carboxylic acids have been prepared. The esters of the 4'-n-alkoxy-biphenyl acids exhibited numerous smectic phases, including the rare smectic F phase. In fact, in this homologous series, all known smectic phases, except the S_{D} phase, are exhibited. From the results, it appears that the trend in the S_{C}-S_{F} transition temperatures for these esters is unaffected by the small changes in molecular structure incurred as the terminal carbon chain is increased. This is in complete contrast to the sensitivity of the S_{C} phases to the structural changes involved as this series is ascended — a sensitivity which is also very marked for the S_{C} phases in other homologous series we have reported previously. Broadly similar results are reported for the corresponding esters of the 4'-n-alkylbiphenyl carboxylic acids.

The F phases of these esters have been shown to be miscible with the smectic F phase of the standard pyrimidine compound first reported by Demus et al., thus confirming the classification of these new S_{F} phases for which photomicrographs of their textures are now presented.

1. Introduction. — Until recently, only 2-(4'-n-pentylphenyl)-5-(4'-n-pentoxyphenyl)-pyrimidine [1] was known to exhibit a smectic F phase. Although extensive studies of this material by physical methods, e.g. X-ray analysis, have revealed some details of the structure of the phase, a full understanding of its nature has yet to be achieved.

In the present study, we have succeeded in preparing a considerable number of new materials that exhibit smectic F phases. Unlike the pyrimidine compound which is difficult to prepare, these esters are readily synthesised by standard procedures. Therefore, these esters now allow us to study the variation in thermal stability of the smectic F phase with changing molecular structure, and, they also provide examples of S_{F} phases which are readily available for study by physical methods.

2. Results and discussion. — 2.1 The 4-(2'-METHYLBUTYL)PHENYL ESTERS OF 4'-n-ALKOXYBIPHENYL-4-CARBOXYLIC ACIDS. — A number of 4-n-alkoxybiphenyl-4-carboxylic acids were esterified with racemic 4-(2'-methylbutyl)phenol. The general structure for these esters is

\[
\text{C}_2\text{H}_{11},\text{O} - \text{C}_4\text{H}_{11}
\]

(*) See note added in proof at the end of this paper.
where \( n = 4-10, 12, 16, \) and 18. The esters with \( n = 7 \) or higher are those which exhibit the smectic F phases. The transition temperatures for these materials are given in table I, and the graphical representation of their transition temperatures against the values of \( n \) is shown in figure 1.

![Plot of transition temperatures against the number of carbon atoms (n) in the n-alkoxy chain of the 4-(2'-methylbutyl)phenyl 4'-n-alkoxybiphenyl-4-carboxylates. Key: \( \bigcirc \), N-I; \( \bullet \), \( S_x \) or N-I; \( \bigtriangleup \), \( S_f-S_C \); \( \times \), \( S_h-S_f \); \( \bigcirc \), \( S_h-S_B \); \( \bigtriangleup \), \( S_B-S_A \); \( \bullet \), \( S_P-S_A \); \( \bigcirc \), crystal-mesophase; \( \square \), mesophase-crystal on cooling.](image.png)

A number of detailed observations can be made from this figure and these may be listed as follows:

a) There is a sudden injection of smectic C properties at the n-hexyloxy ester \( (n = 6) \); this is very similar to the sudden injection of \( S_C \) properties observed in many other similar homologous series \([2, 3]\). All the phases that underlie this tilted \( S_C \) phase are also tilted, whilst in the corresponding temperature range for the n-butyloxy and n-pentyloxy esters, the smectic phases exhibited are orthogonal. It appears that the \( S_C \) phase is the precursor for the formation of the other tilted phases in this particular homologous series.

b) With the exception of the \( S_C-S_A \) transition line, the transition temperature curves for smectic phases occurring at less than 110° have been drawn only through experimental points, i.e. they have not been extended or extrapolated such that each curve becomes vertical at its point of injection (particularly around the region at which the \( S_C \) phase is injected, at \( n = 6 \)). This point is of particular importance when considering the orthogonal B and tilted B \( (S_B) \) transition temperature curves. These two phases have been shown not to belong to the same group \([4, 5]\); therefore the two curves cannot be joined up. However, this suggests that both curves should fall away sharply at a value of \( n \) between 5 and 6. This is not easily represented in a clear manner, particularly for the \( S_B \) transition curve. Therefore, such transition temperature lines have been drawn only from experimental point to experimental point.

c) The \( n \)-butyloxy to \( n \)-nonyloxy esters exhibit nematic phases. The nematic to isotropic liquid transition temperatures alternate in the normal sense \([6]\), with the even members having slightly higher values than the odd members.

d) The \( n \)-butyloxy ester exhibits a \( S_A \) to \( S_B \) transition, but the ester also has latent \( S_h \) properties. Therefore it is possible that the \( S_A \) to \( S_B \) transition may occur via an extremely short-lived \( S_h \) phase.

e) From the \( n \)-heptyloxy ester onwards, all the esters exhibit a well defined smectic F phase, and there was found to be remarkably little variation in the \( S_C \) to \( S_F \) transition temperatures as the series was ascended.

f) The \( n \)-hexyloxy to \( n \)-octadecyloxy esters exhibit tilted smectic B \((S_B)\) phases. The \( S_F \) or \( S_C \) to \( S_h \) transition temperatures decrease in a similar manner to the \( S_A \) to I and \( S_A \) to \( S_C \) transition temperatures as the series is ascended.

g) The \( n \)-heptyloxy to \( n \)-decyloxy esters exhibit smectic G phases below their smectic H phases. Thus, all four materials are pentapolyomorph in their smectic behaviour.

2. Confirmation of the smectic phase types observed. — This section is divided into two parts, one dealing with those esters exhibiting orthogonal phases, and one with those exhibiting tilted phases. We will consider one typical example from each part and describe the results in full.

3. The sequence of tilted phases for the 4-(2'-methylbutyl)phenyl 4'-n-alkoxybiphenyl-4-carboxylates. —

The identification of the phases was achieved using three different techniques:

a) Microscopic textures. — On cooling the isotropic liquid of 4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate a nematic phase was formed. Further cooling resulted in a transition to a smectic phase which exhibited clear fan and homeotropic textures. The phase separated in the form of bâtonnets, indicating that the phase was \( S_A \) in type.

On further cooling, the \( S_A \) phase gave rise to a smectic C phase which exhibited very typical textures — the sanded, the broken fan, and the wizened schlieren texture (Plate 1). Further cooling of this phase
gave a transition (Plate 2) to an unusual phase ($S_p$), which exhibited two types of texture, the chequerboard broken fan texture or the schlieren texture. This schlieren texture (Plate 3) was vastly different from that exhibited by the $S_c$ phase, and was very similar to that reported by Demus and Sackmann [1] for the $F$ phase which they first discovered. The phase appeared to be very fluid and it proved hard to bring it into sharp microscopic focus.

On cooling, this phase gave a transition to a smectic H phase which exhibited two very typical textures — the mosaic (Plate 4) and the broken fan textures. The fan texture did not alter very much from the texture of the preceding $F$ phase, but the change from the schlieren texture of the $F$ phase to the mosaic texture of the $H$ phase was very dramatic.

On cooling the $S_h$ phase, just before the next transition, the mosaic areas became crossed with a number
of parallel lines, giving the impression of a corrugated surface (Plate 5). The mosaic platelets then began to change shape and to give different mosaic areas with smaller, more oblong shapes (Plate 6). The fan texture remained broken and similar to that of the preceding phase. This phase is obviously still tilted in nature, and since it lies below a $S_H$ phase, it was assumed to be $S_G$ in type.

b) Miscibility studies. — A number of miscibility studies were carried out using the $2-(4'-n$-pentylphenyl)-5-(4"-n-pentyloxyphenyl)-pyrimidine as the standard smectic F material. A typical example of a miscibility diagram of state for mixtures of this standard material with 4-(2'-methylbutyl)phenyl 4'-n-decyloxybiphenyl-4-carboxylate is shown in figure 2.

This miscibility diagram of state shows that the test ester exhibits $S_A$ to $S_C$ phases by their co-miscibility with the known phases of the standard pyrimidine. The suspected $S_F$ phase of the test ester is also confirmed as being F in type by its co-miscibility with the F phase of the standard material. It is noted that the supposed $S_G$ phase of the standard material was miscible with the phase of the test ester which forms from the $S_F$ phase on cooling. This phase was shown to be $S_H$ in type by a miscibility study with TBBA similar to that shown in figure 3 for the n-heptyloxy ester. This shows that the pyrimidine in fact has $S_A$, $S_C$, $S_F$, and $S_H$ phases. The miscibility study with TBBA also confirmed that the $S_H$ phase of the test ester gave a $S_G$ phase on cooling, and as can be seen in figure 2, the $S_H$ to $S_G$ transition temperature curve falls away as an increasing amount of the pyrimidine is added.

A complementary miscibility study was carried out with terephthalylidene-bis-4-n-butylaniline (N, $S_A$, $S_C$, $S_H$, $S_G$ and $S_V$ phases) as the standard material and 4-(2'-methylbutyl)phenyl 4'-n-heptyloxybiphenyl-4-carboxylate. The miscibility diagram of state for mixtures of these two materials is shown in figure 3.

This miscibility diagram of state confirms that the test ester exhibits nematic, $S_A$, $S_C$, $S_H$ and $S_G$ phases by their co-miscibility with the corresponding phases.
of TBBA. It also confirms that TBBA has latent SF characteristics [7].

The S_G phases of the n-heptyloxy and n-decyloxy esters were also shown to be miscible, thus confirming that the pyrimidine exhibits a S_4 and not a S_G phase.

By similar miscibility studies, a number of the other esters were shown to exhibit S_F, S_H, and in some cases S_G phases.

c) Differential thermal analysis. — All of the esters were studied by differential thermal analysis. The results for the enthalpy values of the n-octyloxy and n-decyloxy esters are given below; values are in kcal mol⁻¹.

<table>
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<tr>
<th>Ester</th>
<th>ΔH_I or N-S_A</th>
<th>ΔH_S_A-S_C</th>
<th>ΔH_S_C-S_F</th>
<th>ΔH_S_F-S_H</th>
<th>ΔH_S_H-S_G</th>
<th>ΔH_S_G-MP</th>
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<td>(n)</td>
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<td>0.23</td>
<td>0.61</td>
<td>0.44</td>
<td>0.095</td>
<td>1.94</td>
</tr>
<tr>
<td>12</td>
<td>(*)</td>
<td>0.77</td>
<td>(*)</td>
<td>0.32</td>
<td>(*)</td>
<td>4.24</td>
</tr>
</tbody>
</table>

(*) Peak size too small for the enthalpy to be evaluated.

All the other members exhibited the same pattern with respect to the sizes of the enthalpy peaks. The S_A to S_C transitions for all the esters were barely detectable by DTA and similarly, the S_H to S_G enthalpy peaks were hardly discernable. The enthalpy values for the S_C to S_F transitions were however fairly large, indicating first order transitions, whilst the enthalpy values for the S_F to S_H transitions were considerably smaller.

A typical cooling cycle obtained by DTA for the n-octyloxy ester is given in figure 4.

Fig. 4. — Differential thermal analysis (cooling cycle) for 4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate.

4. Confirmation of the phase sequences for the n-butyloxy and n-pentyloxy esters. — Both of these materials exhibit orthogonal smectic phases, and three procedures were again used to identify the phase types.

a) Microscopic textures. — Each ester exhibited a nematic phase which gave a S_A phase on cooling. The S_A phases exhibited the typical clear fan and homeotropic textures. On further cooling, the n-butyloxy ester gave a smectic E phase. The phase was readily characterised by its arced fan and platelet textures. Thus, the n-butyloxy ester exhibits N, S_A, and S_H phases.

On cooling the S_A phase of the n-pentyloxy ester, the fan texture became crossed with transition bars which disappeared on further cooling through 1⁰C. The resultant phase exhibited the clear fan and homeotropic textures, indicating that it is S_B in type. On further cooling, this phase gave rise to a S_E phase which exhibited the typical associated textures.

b) Miscibility studies. — The n-pentyloxy ester was shown to exhibit S_A, S_B, and S_E phases by their separate co-miscibility with the phases of the standard n-decyl 4-(4'-phenylbenzylideneamino)cinnamate (S_A, S_B, and S_E phases).

A similar miscibility study was carried out for the n-butyloxy ester with the standard n-decyl 4-(4'-phenylbenzylideneamino)cinnamate (Fig. 5). This miscibility diagram of state shows that the test ester does exhibit S_A and S_E phases. It also shows that the test ester either has latent S_B properties or that the S_A to S_E transition occurs via an extremely short range S_B phase, i.e., that the transition is S_A-S_B-E.

Fig. 5. — Miscibility diagram of state for mixtures (wt %) of n-decyl 4-(4'-phenylbenzylideneamino)cinnamate (A) with 4-(2'-methylbutyl)phenyl 4'-n-butyloxybiphenyl-4-carboxylate (B).
c) Differential thermal analysis. — Differential thermal analysis was used to confirm the transition temperatures of the two esters. The n-butyloxy ester gave only one enthalpy peak for the transition of the \( S_A \) to the \( S_B \) phase, confirming the situation discussed in b) for this transition.

4.1 The 4-(2'-methylbutyl)phenyl esters of 4'-n-alkylbiphenyl-4-carboxylic acids. — A number of 4-(2'-methylbutyl)phenyl 4'-n-alkylbiphenyl-4-carboxylates were prepared in order to assess the effect of « terminal dipole moments » on the stability of the smectic F phase, by comparison with the alkoxy analogues.

The esters prepared were of the general structure shown in figure 6 with values of \( n = 5-10 \) inclusive. The transition temperatures for these esters are given in table II and a graphical representation of these transition temperatures against the values of \( n \) is given in figure 6.

A number of important features of this plot of the transition temperatures may be listed as follows:

a) There is a sudden injection of smectic C properties at the n-octyl member \( (n = 8) \). All the phases that underlie this \( S_C \) phase are tilted. Earlier members which do not exhibit \( S_C \) phases exhibit only orthogonal phases. The \( S_C \) phase, therefore, again appears to be the precursor for formation of the other tilted phases. Moreover, as these materials do not have terminal outboard dipole moments, as specified in McMillan's model for the C phase [8], the longer chain esters of this series are further examples of materials that do not conform to that theory of the C phase [9]. However, the thermal stabilities of the \( S_C \) phases have decreased considerably by comparison with those of the corresponding alkoxy esters. This suggests that although terminal dipoles are not the primary cause of tilting in the \( S_C \) phase, they do play a part in determining its thermal stability.

b) The n-octyl, n-nonyl, and n-decyl members all exhibit smectic F phases. The thermal stability of these phases have again fallen by comparison with those of the corresponding alkoxy esters. However, the reduction in transition temperature for a \( S_C-S_F \) transition on moving from a n-alkoxy ester to the n-alkyl analogue is not as great as the corresponding drop in the \( S_A \) to \( S_C \) transition temperature. This suggests that the \( S_F \) phase is less effected by terminal dipole moments than the \( S_C \) phase. As in the alkoxy series, the \( S_C-S_F \) transition temperatures appear to be almost unaffected by change in the terminal alky chain length, i.e., the phase is insensitive to small changes in molecular framework.

c) Only the n-nonyl and n-decyl members exhibit smectic G phases, and both of these compounds are therefore pentapolyomorphic with respect to their smectic phase behaviour.

d) The n-pentyl and n-heptyl members exhibit \( S_A, S_B \), and \( S_G \) phases, whilst the n-hexyl member exhibits \( S_A \) and \( S_B \) phases. This is because the n-hexyl member crystallises before a \( S_F \) phase can be formed. Therefore, this ester will have latent \( S_E \) characteristics.

4.2 Confirmation of the smectic phase types observed. — A similar procedure was adopted for the confirmation of the phase types, and to avoid repetition, only a few of the finer points will be discussed.
a) Microscopic textures. — All the textures observed microscopically were similar to those described earlier for the alkoxy series, the only exception occurring with the textures of the $S_F$ phases. These textures were more mosaic-like in character than those of the corresponding alkoxy series, and it is possible that slight differences occur in the structures of the $F$ phases of these two series. It is noted however that the various $F$ phases are all mutually miscible.

b) Miscibility studies. — A number of miscibility studies were carried out with the 2-(4'-n-pentylphenyl)-5-(4'-n-pentyloxyphenyl)-pyrimidine ($S_A, S_C, S_F$, and $S_H$ phases). The n-octyl to n-decyl esters were all shown to exhibit $S_F$ phases.

A miscibility study involving the n-nonyl ester, the test material, with the 4-(2'-methylbutyl)phenyl 4'-n-heptyloxybiphenyl-4-carboxylate ($N, S_A, S_C, S_F, S_H$ and $S_G$ phases) as the standard material was carried out. The miscibility diagram of state for binary mixtures involving these two materials is shown in Figure 7. This study shows that the test ester does exhibit $N, S_A, S_C, S_F, S_H$, and $S_G$ phases by their separate co-miscibility with the known phases of the standard material.

c) Differential thermal analysis. — Differential thermal analysis was used to confirm the transition temperatures for the phase changes observed microscopically for all the materials. The enthalpy peaks for the $S_A$ to $S_C$ and $S_H$ to $S_G$ phase changes were extremely small suggesting that both transitions are of the second order or weak first order kind.

4.3 Preparation of materials. — The synthesis of these esters involved the preparation of the acid and phenol moieties. Firstly we will deal with the synthesis of racemic 4-(2'-methylbutyl)phenol.

a) Preparation of 2-methylbutyric acid. — To a solution of potassium permanganate (42 g, 0.29 mol) and sodium hydroxide (6 g, 0.15 mol) in water (1.5 l), 2-methylbutan-1-ol (25 g, 0.28 mol) was added with stirring. The mixture was cooled in an ice bath for 1 h. The mixture was allowed to come to room temperature and stirred for a further 24 h. Potassium permanganate (14 g, 0.09 mol) was then added to the mixture and the resulting suspension was stirred for a further 24 h. Sodium metabisulphite was added to destroy the excess of potassium permanganate and the solution was brought to a pH of 9 by addition of 5 % sodium hydroxide solution. The mixture was then filtered, and the solid collected was washed with 5 % sodium hydroxide solution. The filtrate was then washed with ether (2 x 30 ml) and the aqueous layer was acidified with concentrated hydrochloric acid. The solution was then extracted with ether (2 x 50 ml), and the extract was dried over anhydrous sodium sulphate. The ether was evaporated off and the resultant liquid distilled, the fraction boiling at 148-149$^\circ$C/15 mm Hg being collected. The yield of 2-methylbutyric acid was 12 g, 41.5 %.

b) Preparation of 4-(2'-methylbutanoyl)anisole. — Firstly, 2-methylbutanoyl chloride was prepared by heating under reflux 2-methylbutyric acid (12 g, 0.12 mol) and an excess of thionyl chloride (60 ml) for 1 h. The excess of thionyl chloride was removed by fractional distillation and the remaining acid chloride was distilled, the fraction boiling at 114-115$^\circ$C being collected. The yield was 6.1 g (42 %).

The acid chloride (6.1 g, 0.05 mol) was added dropwise to a stirred suspension of freshly crushed aluminium trichloride (10 g, 0.075 mol) and anisole (6.5 g, 0.6 mol) in dry light-petrol (bp 40-60$^\circ$C) (50 ml) at 0$^\circ$. The mixture was stirred at 0$^\circ$ for 6 h and then allowed to come slowly to room temperature over a further 12 h. The complex was destroyed by the addition of crushed ice (50 g) and concentrated hydrochloric acid (10 ml). To this mixture chloroform (20 ml) was added to further facilitate the destruction of the complex.

The resultant mixture was shaken with chloroform (2 x 30 ml). The combined extracts were washed with water (2 x 15 ml) and then dried over anhydrous sodium sulphate. The chloroform was removed by evaporation and the resultant oil was distilled.
The fraction boiling at 152-153°C/1 mm Hg was collected. The yield was 5.5 g (57%). This product gave the correct mass ion and its infra-red spectrum was consistent with the required structure.

c) Preparation of 4-(2'-methylbutyl)phenol. — Stage (i): A solution of anhydrous aluminium trichloride (21 g, 0.157 mol) in super dry ether (60 ml) was added dropwise to a mixture of lithium aluminium hydride (3 g, 0.071 mol) and super dry ether (60 ml). A solution of 4-(2'-methylbutanoyl)anisole (5.5 g, 0.028 mol) in chloroform (100 ml) was then added over a period of 30 min. The mixture was stirred and heated under reflux for 18 h. The excess of lithium aluminium hydride was destroyed by the cautious addition of water (100 ml); then a 38% solution of hydrochloric acid in water (72 ml) was added. The ether layer was separated and washed successively with water (3 x 100 ml), brine (3 x 100 ml), and water (100 ml). It was then dried over anhydrous sodium sulphate. The ether was removed by evaporation and the residue was distilled. The product was found, by infra-red spectroscopy, to be a mixture of the alkylphenol and the alkylanisole. Because the phenol is the ultimate product required, no attempt was made to separate the 4-(2'-methylbutyl)anisole from the demethylated material.

Stage (ii): The mixture from the previous stage was carefully added to a solution of acetic acid (100 ml) and aqueous hydrogen bromide (48% w/w, 150 ml). The mixture was cooled and poured into a mixture of ice (50 g) and water (50 ml). The mixture was stirred for 30 min and the resulting solution was shaken with chloroform (2 x 30 ml). The extracts were washed with water (1 x 15 ml) and then dried over anhydrous magnesium sulphate. The chloroform was removed by evaporation, the residue was distilled and the fraction boiling at 110-120°C/2 mm Hg was collected. The yield was 3 g (60.5% based on the initial ketone). The structure and/or purity of the product were confirmed by mass spectrometry, infra-red analysis, and glc.

The known acids which were required were prepared by two methods; the acids with alkyl chains and those with shorter terminal alkoxy chains were synthesised by preparing the 4-n-alkoxy- and 4-n-alkyl-4'-bromobiphenyls by standard methods. These were then cyanated and the resulting cyanides were hydrolysed [10]. However, for the n-decylxoy acid onwards, the cyanide proved to be very resistant to hydrolysis. Therefore, an alternative method was developed. The acids were prepared directly from the corresponding bromo-compounds by carbonation of the Grignard reagents prepared by the entrainment method [11].

d) Preparation of the esters. — All the esters were prepared using the boric acid method [12].

To the acid (0.003 mol) dissolved in toluene (30 ml), a solution of the phenol (0.64 g, 0.0036 mol) in toluene (30 ml) was added. To the resulting solution, concentrated sulphuric acid (0.2 ml) and boric acid (0.1 g) were added. The mixture was then heated under reflux and the water produced in the reaction was removed by azeotropic distillation using a Dean and Stark apparatus. After continuing this process for 24-48 h, the solvent was evaporated off, and the residue was taken up in chloroform (10 ml). This solution was then used to chromatograph the product on silica gel (80-200 mesh, 2.5 x 30 cm), using a mixture (1:1) of chloroform and light-petrol (bp 40-60°C) as eluant. Individual fractions were tested by tlc, and the combined fractions containing the ester (single-spot material) were evaporated to dryness. The residue was then crystallised from ethanol until the product gave a constant melting point and transition temperatures.

The structures and/or purities of the products were checked by infra-red spectroscopy, mass spectrometry and tlc. Satisfactory elemental analysis for all the products were also obtained. The transition temperatures for the esters are given in tables I and II.

4.4 Physical Measurements. — The determination of the transition temperatures for the pure materials and binary mixtures in miscibility studies were made using a Nikon polarising microscope in conjunction with a Mettler FP52 heated stage and control unit. Checks on transition temperatures and measurements of enthalpies of transition were made using a Stanton Redcroft low temperature differential thermal analyser-model 671B.

4.5 Optically Active Analouges. — Only the racemic materials have been discussed here. Some analogous optically active esters will be discussed by McDonnell and Gray in a further publication.

5. Conclusions. — 1) These readily accessible materials provide further examples of smectic F compounds. The pentapolymeric materials give the thermodynamic ordering of the various smectic phases as \( S_A, S_C, S_F, S_H, S_G \). It has been shown that the \( S_G \) phase is of higher thermal stability than the \( S_C \) phase [13] and that the \( S_P \) phase is of higher thermal stability than the \( S_H \) phase [4, 5] giving the overall sequence as \( S_A, S_D, S_C, S_F, S_H, S_H, S_E, S_G \) [14]. The only doubt attached to this sequence concerns the \( S_E \) phase which has been placed above the \( S_C \) phase only because the orthogonal analogues of other tilted phases appear to have the higher thermal stabilities.

2) Unlike the \( S_C \) phase, the \( S_F \) phase is hardly affected by small changes in molecular structure. Also, the \( S_F \) phase appears to be very fluid compared with the \( S_H \) phase. These two observations suggest
SMECTIC F TRENDS IN 4-(2'-METHYLBUTYL)PHENYL ESTERS

Transition temperatures (°C) for compounds of structure

\[
C_nH_{2n+1}O-H(C_8H_{17})-O-CH_2CH(CH_3)C_2H_5
\]

<table>
<thead>
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<th>I-N</th>
<th>I or N-S_A</th>
<th>S_A-S_C</th>
<th>S_C-S_F</th>
<th>S_F-S_H</th>
<th>S_H-S_G</th>
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</table>

( ) Monotropic transition temperature.

Note added in proof. — It should be emphasised that there is no disagreement between the results given in this paper and those reported by H. Sackmann in his paper on The Stand of the System of Smectic Liquid Crystals by miscibility measurements which also appears in these proceedings. Both investigations show that the tilted, hexagonally ordered smectic phase which succeeds the \( S_c \) phase of TBBA on cooling is immiscible with orthogonal, hexagonally ordered smectic phases, i.e., with the \( S_B \) phase. In both pieces of work, this tilted, hexagonally ordered phase of TBBA has been shown by miscibility methods to be of the same type as the phase which succeeds the \( S_F \) phase of the pyrimidine on cooling. The apparent differences are entirely ones of nomenclature.

In this paper, we call the tilted, hexagonally ordered phases of TBBA and the pyrimidine \( S_B \), whereas...
Sackmann calls them \( S_6 \). Consequently, a reversed nomenclature has arisen for the next smectic phase which succeeds the tilted, hexagonally ordered smectic phase of TBBA on cooling. We call this \( S_{og} \), whereas Sackmann calls it \( S_{oh} \).

In summary, our nomenclature gives the following phase sequences:

- TBBA: I, N, \( S_A \), \( S_C \), \( S_H \), \( S_G \)
- Pyrimidine: I, \( S_A \), \( S_C \), \( S_F \), \( S_H \)

Sackmann's nomenclature gives:

- TBBA: I, \( S_A \), \( S_C \), \( S_G \), \( S_H \)
- Pyrimidine: I, \( S_A \), \( S_C \), \( S_F \), \( S_G \)

There is however no disagreement concerning the natures of these phases for which we have simply used different code letters.

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References