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MOLECULAR STRUCTURE AND THE POLYMORPHISM OF SMECTIC LIQUID CRYSTALS

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Abstract. — The smectic properties of four series of esters — the methyl to n-decyl esters of the 4'-n-hexyloxy-, 4'-n-heptyloxy-, 4'-n-octyloxy- and 4'-n-nonyloxy-biphenyl-4-carboxylic acids — are discussed. The effects on the smectic phases of increasing the alkyl chain lengths are quite striking, particularly in the last three of these series, where Sc properties are introduced for the middle members. The SC-SA transition temperatures in each series lie on two parabolae with the result that the earlier homologues exhibit A, B, E sequences and the higher homologues form only SA phases. Thus, the tendency of these series to exhibit Sc phases is a function of alkyl chain length and is not determined simply by the more rigid central part of the molecule containing the permanent dipole moments. Evidence for the Sc properties of these esters is given in detail. Other cases in which increasing the alkyl chain length leads to marked changes in smectic polymorphic behaviour, including the sudden injection of different smectic polymorphic phases into particular sequences of smectic phases, are reviewed.

1. Introduction. — Previous studies [1] of substituted and unsubstituted o-phenylalkyl esters of 4-(4'-phenylbenzylideneamino) — cinnamic acid — structure I — have shown that features of molecular structure which deviations from molecular linearity when the number of methylene groups is odd, i.e., when \( n \) in (I) is odd, the thermal stabilities of the B and E phases are enhanced and the thermal stability of the A phase is lower \( S_A-I \) transition temperatures lead to increases in \( S_B-S_A \) and \( S_E-S_B \) transition temperatures and vice versa. Such effects are illustrated in figure 1, where it is shown that the alternation in \( S_A \) thermal stability as the series is ascended is accompanied by a reversed alternation in both \( S_B \) and \( S_E \) thermal stabilities. The extent of the alternation is such that for the second member of the series, the thermal range of the \( S_A \) phase is effectively zero, and a direct I-\( S_{AB} \) transition takes place.

Such effects have been interpreted [1] in terms of

\[
\text{CH} = \text{N} - \text{CH} = \text{COO(CH}_2\text{)}_n \text{X}
\]

(Where \( X \) may be \( H, \text{CH}_3 \) or \( \text{Cl} \) in the 3- or 4- position)

I

decreased, relative to members of the series for which \( n \) is even.

Recently we have developed our ideas about these observations considerably, but since our thinking has been greatly influenced by advances in knowledge of the structures of \( S_B \) and \( S_E \) phases which will be reported in other papers presented at this meeting, we have decided not to say more on this aspect at present. We simply wish to remind the reader of these observations which show clearly that small changes in molecular architecture can markedly affect the smectic poly-
morphic situation in a compound — in this case, in relation to the $S_A$, $S_B$ and $S_E$ phases.

To this reminder, we would now add an account of recent experimental results which further emphasise the quite subtle way in which the incidence of different smectic polymorphic forms exhibited by compounds can be affected by minor changes in their molecular structures. Indeed, most of the results to be discussed relate to the effects of merely lengthening a simple n-alkyl chain.

The observations should serve as a warning against our assuming (a) that we know everything about a particular smectic phase simply because a satisfactory structure for it has been obtained by physical studies of one or possibly two or three materials or (b) that theoretical models for certain smectic polymorphs based on the commonest types of structure to exhibit these phases are necessarily completely satisfactory.

2. Results and discussion. — The results presented are concerned with the incidence of tilted $S_C$ phases in homologous series of n-alkyl 4'-n-alkoxybiphenyl-4-carboxylates.

Figure 2 presents the results obtained for the esters of 4'-n-octyloxybiphenyl-4-carboxylic acid. Features of particular interest may be listed as follows:

1) The thermal stabilities ($S_A$-$I$ transition temperatures) of the $S_A$ phases fall-off quite sharply at first and then much more gently as the alkyl chain lengths. There is a regular alternation of the $S_A$-$I$ temperatures.

2) The thermal stabilities of the $S_B$ and $S_E$ phases fall-off very steeply indeed as the alkyl chain lengthens, and neither phase occurs after the n-propyl ester.

3) The methyl ester does not exhibit a $S_A$ phase and the transition observed on cooling the isotropic liquid is classed as $I$-$S_{AB}$.

4) The n-octyl, n-nonyl and n-decyl esters exhibit only $S_A$ phases.

5) The n-butyl ester exhibits a well defined $S_A$ phase when the $S_A$ phase is cooled — coincidentally this transition occurs at the same temperature as that at which the crystal melts to the $S_A$ phase on heating. The $S_A$-$S_C$ transition temperatures plotted in figure 2 for the n-pentyl, n-hexyl and n-heptyl esters are *vita* monotropic transition temperatures obtained by extrapolations of transition lines in diagrams of state obtained from miscibility experiments — see later figures.

The results for this series therefore show that lengthening of the alkyl chain strongly disfavours $S_B$ and
S₈ phases, but that this structural change much less adversely affects the S₄ phase. This behaviour is reminiscent of the different effects on the thermal stabilities of S₈ phases and of S₆ and S₇ phases observed for the ω-phenylalkyl esters mentioned in the introduction.

However, the most striking and surprising feature of this series is unquestionably the sudden injection of S₆ properties at the n-butyl ester and the fact that the observed S₆-S₈ transition temperature for this ester and the virtual S₆-S₈ temperatures for the near homologues apparently constitute two parabolae resulting from an alternation of these temperatures as the n-alkyl chain is lengthened. We therefore sought confirmatory evidence for this behaviour from as many sources as we could.

2.1 Confirmatory evidence for the S₆ properties in n-alkyl 4'-n-alkoxybiphenyl-4-carboxylates

— 2.1.1 Studies of related homologous series. — Figure 3 presents results for the n-alkyl 4'-n-heptyloxybiphenyl-4-carboxylates. Features (1) to (5) listed for the octyloxy series again occur (cf. Fig. 2). Thus, the methyl ester exhibits an I-S₆ transition and the thermal stabilities of the S₆ and S₇ phases fall-off steeply as the n-alkyl chain lengthens. Moreover, for the n-butyl ester, a monotropic S₆-S₈ transition occurs, and for the next three higher homologues, virtual S₆-S₈ transitions are indicated, such that the S₆-S₈ temperatures alternate and constitute two parabolae.

Figure 4 presents results for the n-alkyl 4'-n-hexyloxybiphenyl-4-carboxylates. The situation is now different, there being no evidence for any S₆ properties in

![Figure 3](image)

![Figure 4](image)

![Figure 5](image)
this series. There is an obvious connection between the absence of $S_c$ properties and the fact that the $S_b-S_a$ transition temperatures fall away much less steeply in this series as the $n$-alkyl chain lengths. As a result, $S_a-S_b$ transitions are observed (although most of the $S_b$ phases are monotropic) for all members up to the $n$-decyloxy chain. Thus, with the shorter $n$-hexyloxy chain, the system prefers to form orthogonal $S_b$ phases direct from the $S_a$ phase, irrespective of the length of the ester alkyl chain.

It is noted that the first member of the series again gives a direct I-$S_{AB}$ transition and that the expected [1] opposite alternation sense of the $S_a$-I and the $S_b$-$S_a$ transition temperatures is clearly shown. The thermal stability of the $S_b$ phase again falls-off very steeply as the alkyl chain lengthens.

Figure 5 presents results for the $n$-alkyl 4'-n-nonyloxybiphenyl-4-carboxylates. The general pattern of behaviour is now similar to that for the heptyloxy and octyloxy series, the injection of $S_c$ properties being observed once again. The shapes of the two parabolae on which the $S_c-S_a$ transition temperatures lie are more similar to those in the heptyloxy series, possibly suggesting some alternation effect on the $S_c$ properties as the $alkoxy$ chain is extended. As in the other two series (Figures 2 and 3), the $S_c$ phase is actually observed for only the $n$-butyl ester, but the measurement of virtual $S_c-S_a$ temperatures for the next three

<table>
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<th>$C_nH_{2n+1}$</th>
<th>$S_a$</th>
<th>$S_b$</th>
<th>$S_c$</th>
<th>$S_a$</th>
<th>$S_b$</th>
<th>$S_c$</th>
<th>$S_a$</th>
<th>$S_b$</th>
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<tr>
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( ) Monotropic transition.
(*) Virtual transition temperature.
(**) $S_{AB}$-I.

---

**Table I**

*Transition temperatures in °C for the compounds of structure*  
$C_6H_{13}$

<table>
<thead>
<tr>
<th>$C_nH_{2n+1}$</th>
<th>$C \rightarrow S$</th>
<th>$S_c \rightarrow S_b$</th>
<th>$S_b \rightarrow S_a$</th>
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<th>Recryst. Temp.</th>
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<td>$C_6H_{13}$</td>
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<td>132</td>
<td>—</td>
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<td>$C_7H_{15}$</td>
<td>74</td>
<td>—</td>
<td>84</td>
<td>64</td>
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<tr>
<td>$C_8H_{17}$</td>
<td>74</td>
<td>—</td>
<td>82</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>$C_9H_{19}$</td>
<td>71</td>
<td>—</td>
<td>80</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>$C_{10}H_{21}$</td>
<td>59</td>
<td>—</td>
<td>78</td>
<td>51</td>
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( ) Monotropic transition.
(*) Virtual transition temperature.
(**) $S_{AB}$-I.

---

**Table II**

*Transition temperatures in °C for the compounds of structure*  
$C_7H_{15}$

<table>
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<tr>
<th>$C_nH_{2n+1}$</th>
<th>$C \rightarrow S$ or I</th>
<th>$S_c \rightarrow S_b$</th>
<th>$S_b \rightarrow S_a$</th>
<th>$S_a \rightarrow I$</th>
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( ) Monotropic transition.
(*) Virtual transition temperature.
(**) $S_{AB}$-I.
STRUCTURE AND POLYMORPHISM OF SMECTIC LIQUID CRYSTALS

Table III

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<th>CₙH₂ₙ₊₁</th>
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<th>Sₘ → Sₚ</th>
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<td>82</td>
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<td>(46)</td>
<td>(*)</td>
<td>(83)</td>
<td>79</td>
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<td>—</td>
<td>79</td>
<td>69</td>
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( ) Monotropic transition.
(*) Virtual transition temperature.
(**) Sₘ→I.

Table IV

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<tr>
<th>CₙH₂ₙ₊₁</th>
<th>C → S or I</th>
<th>Sₐ → Sₜ</th>
<th>Sₚ → Sₐ</th>
<th>Sₙ → Sₚ</th>
<th>Sₘ → Sₚ</th>
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<td>—</td>
<td>—</td>
<td>(**) 82</td>
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( ) Monotropic transition.
(*) Virtual transition temperature.
(**) Sₘ→I.
(*** ) Virtual transitions — temperatures to be determined — approx. values are given by extrapolating the Sₘ→I curves on figure 5.

higher homologues and for the octyl ester in the nonyloxy series suggests that a gradual displacement of the Sₙ parabolae to higher ester alkyl chain lengths may be occurring as the alkoxy chain is extended.

Three of the four series of n-alkyl 4'-n-alkoxybiphenyl-4-carboxylates therefore provide evidence for the injection of Sₙ phases in the middle members of the series, and the fourth series (n-hexyloxy) differs with regard to the trends in Sₚ thermal stabilities in a manner such that the observation of Sₙ phases could not be anticipated. The observed transition temperatures for these four series of esters are listed in tables I to IV.

2.1.2 Microscopic observations of the smectic phase textures. — Confirmatory evidence for the occurrence of Sₙ phases in certain members of the series of esters was provided by microscopic observation of the textures of the smectic phases. The Sₙ and Sₚ phases had typical focal-conic fan textures. The transition between these phases is not however easy to detect microscopically since the transition bars which usually mark Sₙ→Sₚ transitions are barely discernable or not observed at all. The Sₚ phases had focal-conic fan textures crossed by well defined concentric arcs. Areas of the Sₙ phases were however often found to be homeotropic. When the transition to the Sₚ phase had occurred, these areas
remained homeotropic, and the homeotropic areas of both phases gave uniaxial interference figures on conoscopic observation. When a homeotropic $S_b$ area was cooled into the temperature range of the $S_e$ phase however, it immediately showed birefringence and developed the platelet texture [2] of the $S_e$ phase. The platelet textures of all the $S_e$ phases were shown to give biaxial interference figures. The microscopic properties of the $S_a$, $S_b$ and $S_e$ phases were therefore quite typical.

In the case of the butyl esters of the heptyloxy, octyloxy and nonyloxy series, cooling of the $S_a$ phase gave strong confirmatory evidence for the $S_e$ phases. If the $S_a$ phase had a fan texture, the broken fan texture of the $S_c$ phase was formed. If the $S_a$ phase had a homeotropic texture, the birefringent, biaxial Schlieren texture of the $S_c$ phase was formed.

Plates 1 to 4 illustrate the most important of the above textural features of the $S_e$ and $S_c$ phases.

2.1.3 Miscibility studies. — A large number of diagrams of state for mixtures of the various esters with one another and with a number of standard materials exhibiting authenticated smectic phases of various types were obtained. Thus co-miscibility of all the $S_a$, $S_b$ and $S_e$ phases with standard phases of these types was proved.

The methyl esters were studied particularly closely, and figure 6 shows the diagram of state for mixtures of one of these methyl esters with a standard material exhibiting $S_a$, $S_b$ and $S_e$ phases. As can be seen, the $S_a$ phase of the standard material can no longer be detected once the concentration of the methyl ester has exceeded about 75%. The asymptotic approach of the $S_a$-I and $S_b$-$S_a$ transition lines across the diagram of state does not suggest that the $S_a$ phase becomes monotropic with respect to the $S_b$ phase, and so the transition for the methyl ester is classed as $S_{AB}$-I. Effectively however, the $S_b$ phase forms direct from the isotropic liquid.

Figure 7 demonstrates the co-miscibility of the $S_c$ phase of the standard material 4-n-octyloxybenzoic acid with the smectic phase formed by cooling the $S_a$ phase of n-butyl 4'-n-octyloxybiphenyl-4-carboxylate. Figure 8 shows that the $S_c$ phase of this same ester is immiscible with the standard $S_b$ phase of n-nonyl 4-(4'-phenylbenzylidene amino) cinnamate; the iden-

Plate 1. — Focal-conic fan texture of the $S_e$ phase of methyl 4'-n-octyloxybiphenyl-4-carboxylate showing the well defined concentric arcs crossing the fan-shaped areas ($\times$ 200).

Plate 2. — The $S_b$ phase of methyl 4'-n-octyloxybiphenyl-4-carboxylate ($\times$ 200). In this case, most of the higher temperature $S_b$ phase from which the $S_e$ phase was obtained by cooling was homeotropic. Most of the $S_e$ phase therefore exists in the platelet texture from which a biaxial interference figure is observed and only small areas appear as fans with concentric arcs as in Plate 1.
tity of the smectic phase as a $S_C$ phase is therefore confirmed.

Figure 9 shows the diagram of state for mixtures of the n-butyl and n-hexyl esters of 4'-n-octyloxybiphenyl-4-carboxylic acid. The $S_C-S_A$ transition line *rises* across the diagram from the standard ester indicating that the latent $S_C$ properties of the n-hexyl ester are more pronounced than those of the n-butyl ester. Extrapolation therefore gives a higher $S_C-S_A$ transition temperature for the n-hexyl ester than that for the n-butyl ester. Direct observations of the $S_C$ properties of the n-hexyl ester are therefore prevented solely by the failure of the $S_A$ phase to supercool adequately before crystallisation occurs. Other virtual $S_C-S_A$ transition temperatures recorded in figures 2, 3 and 5 and in tables II, III and IV were obtained from similar extrapolations across the appropriate diagrams of state.

2.1.3 *Differential thermal analysis.* — In the case of all three n-butyl esters for which $S_C$ phases could be detected by microscopy, the cooling cycles in each case gave peaks for the $I-S_A$ and $S_A-S_C$ transitions, followed by a large peak for the crystallisation process. Reheating *before* the onset of crystallisation gave the same peaks for the $S_C-S_A$ and $S_A-I$ transitions and from these, enthalpy values were obtained. The enthalpies for the $S_C-S_A$ transitions were smaller (0.25 to 0.50 kcal mol$^{-1}$) than those for the $S_A-I$ transitions (1.2 to 1.7 kcal mol$^{-1}$).

The conclusion we must reach from these studies is therefore that the tendency of the n-alkyl 4'-n-alkoxybiphenyl-4-carboxylate system to exhibit particular sequences of smectic phases — either A, B, E (or part of this sequence) or A, C is a function of alkyl chain length and is not determined simply by the core structure containing the permanent dipole moments. The explanation of this situation is not straightforward, and we do not feel that the ideas we have about it are either sufficiently developed or adequately tested to commit them to print at present. What does seem to emerge however is that the McMillan theory [3] of the $S_C$ phase based on permanent dipole moments in the molecules is not the final or complete answer to an understanding of this particular smectic phase and why it occurs.

In the light of these results, it is interesting to look at other series of compounds to see whether similar or related phenomena have been observed, i.e., to see whether, in addition to regular trends in transition temperatures along homologous series, there is evi-
A very close analogy to the behaviour now reported for the n-alkyl 4'-n-alkoxybiphenyl-4-carboxylates is probably provided in the recent report by Smith et al., [4] of the smectic polymorphism in series of Schiff's bases of the structure shown in figure 10.
Although the identities of some of the phases (S, S₃, S₅) remain in doubt, and the authors themselves put a question mark after their assignment of certain S phases to the C category, there is little doubt in our minds that photomicrographs that have been published [5] for these phases show that they are of the S₅ type. If this is so, we therefore have further examples of the sudden injection of S₅ phases into Schiff's base systems which are otherwise predominantly Sₐ, Sₖ (and probably Sₐ, Sₖ, S₃) in their sequences. Moreover, it is possible that the occurrence of the phases in alternate members (see Fig. 10) can be explained by an alternation in thermal stability of the S₅ phases of the kind illustrated in figures 2, 3 and 5. Again therefore, while the more rigid central core structure of the molecule is retained constant and the length of the terminal n-alkyl chain is altered, different smectic polymorphic forms are observed.

A further instance of phase injection occurs in the well-known series [6] of 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids (II).

![Chemical structure](image)

When the alkyl chain is extended to C₁₆H₃₃, the injection of a S₎ phase into a Sₐ, S₅ sequence of phases for the earlier homologues is observed. The attainment of this particular chain length is therefore the trigger for the change of sequence of phases on heating from Sₕ, Sₐ to Sₕ, Sₖ, Sₐ.

Also of relevance are our own observations [7] on the effects of the nature of the terminal substituent (X) on the smectic polymorphism observed in some 4-(4'-substituted benzylideneamino)-4'-octyloxybiphenyls of the structure shown in figure 11. We are not now comparing members of a homologous series, but it is interesting to note that the compounds fall into two categories — those giving a Sₐ, Sₖ, S₈ sequence of phases and those giving a Sₐ, Sₕ, Sₕ or a Sₕ, Sₖ sequence of phases on cooling. Although the number of substituents used is rather limited, it seems significant that the A, B, E sequence occurs when the terminal group X is globular, i.e., symmetrical in shape about the ring-X bond. However, when the substituent X is bent with respect to this bond, the A, C, B or C, B sequence occurs. Thus with X=CH₃ and X=CH₂H₂ we have the first two members of a homologous series. With X=CH₃ (globular), the sequence is N, A, C, B, but on moving to the ethyl homologue, the N, A, C, B sequence arises. Thus, an Sₕ phase has been injected. These Schiff’s bases therefore provide a further example of the type reported for the esters.

The necessity for a globular substituent X in order to obtain the A, B, E sequence can, we think, be rationalised in terms of recent developments relating to molecular motion permitted in the Sₕ phase. However, the occurrence of Sₕ phases with the bent terminal groups, as with the sudden injection of Sₕ and Sₖ phases at particular points in other homologous series, needs more thought and experimentation before secure explanations of this behaviour can be proposed.

Nonetheless, these various observations show rather nicely how finely balanced the smectic polymorphic situation in compounds can be, and how readily this balance can be disturbed by quite minor molecular structural changes. Until we can understand these effects, we are not in a position to predict with any certainty how smectic polymorphism will change on passing from any one compound to another, but until we can do this we cannot pretend that we really comprehend smectic liquid crystals.

3. Experimental section. — 3.1 Preparation of materials. — The n-alkyl 4'-alkoxybiphenyl-4-carboxylates and the 4-(4'-substituted benzylideneamino)-4'-n-octyloxybiphenyls were prepared by fairly standard methods. Details of these procedures and the criteria of purity of the compounds (from elemental analysis, mass spectrometry, gas-liquid chromatography and infra-red spectroscopy) will be published later.
3.2 Physical Measurements. — Observations of microscopic textures and measurements of transition temperatures for both the pure esters and their mixtures were carried out using a Nikon polarising microscope in conjunction with a Mettler FP 52 heated stage and control unit. Tables I to IV list the transition temperatures. Checks on transition temperatures and measurements of enthalpies of transition were made using a Stanton Redcroft low temperature differential thermal analyser — model 671 B.

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