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NOVEL SMECTIC POLYMORPHIC BEHAVIOUR IN HOMOLOGOUS SERIES OF MESOGENS

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Abstract. — The high alternation of nematic thermal stabilities found in the series of \( \omega \)-phenylalkyl 4-(4'-phenylbenzylideneamino) cinnamates as the homologous series was ascended has been further exaggerated by substituting the terminal phenyl ester ring with methyl or chloro substituents in the 3'- or 4'-positions. Nematic phases were found only when an even number \( n \) of methylene units occurred in the alkylene chain.

Smectic thermal stabilities also alternated as each of the four series of esters was ascended. However, the smectic A thermal stabilities decreased and the smectic B thermal stabilities increased on passing from even to odd values of \( n \). In some cases this caused the thermal stabilities of the smectic A and B phases to coincide for odd values of \( n \). When this occurred, a unique texture was observed microscopically at the I-S transition. Although no S\( \alpha \)-S\( \beta \) transition could be detected microscopically or by D. T. A., miscibility studies indicated that a transitional S\( \alpha \) phase still existed. This suggests that it is necessary to form a transitional S\( \alpha \) phase intermediate between the amorphous liquid and a S\( \beta \) phase, both on heating and cooling. This transition has been called S\( \alpha \)-S\( \beta \)-I.

Smectic E phases were also found for many of the sixteen new esters, and the thermal stabilities of S\( \alpha \) phases, like those of S\( \beta \) phases, increased for odd values of \( n \).

The relative effects of 3'- and 4'-methyl- and chloro-substituents on N, S\( \alpha \), S\( \beta \) and S\( \epsilon \) thermal stabilities are discussed.

\[ X - (\text{CH}_2)_n - \text{CH} = \text{N} - (\text{CH}_2)_n - \text{CH} = \text{CH} - \text{CO} - \text{O}(\text{CH}_2)_n \]
n-alkyl esters, sometimes led to alternations in phase type as the series were ascended, i.e., from smectic + nematic to smectic and back to smectic + nematic on passing from one member to another. The high alternation in N thermal stability in these series was attributed to the fact that as the series were ascended, the spatial disposition of a bulky terminal ester phenyl ring was being altered (Fig. 1) relative to the rest of the molecule, and not merely that of a small terminal methyl group as in the case of an homologous series of n-alkyl compounds, i.e., the molecules alternate between being lath-shaped and L-shaped.

Particularly when the substituent X in structure (I) was a phenyl group, smectic polymorphism occurred. The thermal stabilities of both smectic A (Sₐ) and smectic B (Sₐ) phases also alternated, but to a much smaller extent; the alternations of the transition temperatures Sₐ-N or I and Sₐ-Sₐ were in fact of opposite senses. These smaller alternations were also accounted for in terms of molecular shape. Smectic E (Sₑ) phases were commonly exhibited on cooling the Sₐ phases.

In the present work, we have again used a phenyl group as the substituent X, but by substituting the ester ring in the 3''- or 4''-position (Fig. 1) with either a methyl or a chloro substituent, the degree to which the substituted ring lies off-axis for odd values of n may be enhanced, i.e., the molecules should deviate more from being lath-like in shape. If the explanations of Gray and Harrison are correct, even more dramatic alternations in N thermal stabilities should therefore be observed [3], but the S thermal stabilities should be affected much less.

It is noted that a 3''-substituent in the ester ring in fact may adopt two extreme spatial positions when the ring is coplanar with the rest of the molecule, because of possible rotation about the CH₂-Ph (or O-Ph) bond. It was considered that the present studies might give information about the significance of such rotational motions in liquid crystals, and that a comparison of the properties of chloro and methyl substituted isomers might be instructive, as these two substituents are of similar sizes, but quite different dipolarities.

Results and discussion. — Details relating to the mesomorphic properties of the sixteen new 3''- and 4''-methyl- and chloro-phenyl and -o-phenylalkyl 4-(4'-phenylbenzyldieneamino) cinnamates (see Fig. 1) are given in Table I and depicted graphically in figures 2, 3, 7, 8. The unsubstituted homologues studied earlier [1, 2] are included in the Table for comparison; these four esters were re-examined in this work and additional data relevant to the Sₑ phase are listed. These unsubstituted homologues exhibit at the most smectic A and smectic B phases, and a similar polymorphism was expected and occurred for the 3''- and 4''-substituted esters. However, some unique features were found. These will now be discussed and an attempt made to rationalise the observations because of the systematic nature of the compounds selected for study.

Nematic-isotropic liquid transition temperatures. — The situation with regard to the N-I transition temperatures may first be dealt with briefly, because it is closely similar to that found and already reported [3] for the analogous compounds with X = CN. With X = Ph, the compounds with even values of n (0 and 2), whether substituted or not in the 3''- or 4''-positions, are essentially lath shaped and exhibit N phases of
Novel Smectic Polymorphism in Homologous Series

Temp (°C)

Fig. 2. — Plot of liquid crystal transition temperatures against n, the number of methylene units in the alkylene chain for the 3'-methyl-o-phenylalkyl 4-(4'-phenylbenzylideneamino) cinna-mates

Key: (△), N-I; (○), Sx-I or N; (□), C-Sx, Sb or I;
(□□), SAB-I; (●), Sb-SA; (■), Sb-Sb.

High thermal stability. The order for the N-I temperatures is 4' > unsubstituted > 3', since the 4'-substituent elongates the molecule, whereas the 3'-substituent slightly broadens it, irrespective of which spatial position it occupies (see Fig. 1). When n is odd, the unsubstituted esters do not exhibit nematic phases because of the severe departure from lath-like shape which the molecules experience as a result of the protrusion of the phenyl ring from the cylinder defining the rest of the molecule. Introduction of a 4'-substituent accentuates this situation as does that of a 3'-substituent, provided that it resides for some time in the spatial position which further enhances the L-shaped nature of the molecule (see Fig. 1). Consequently, in all these cases having odd values of n, very low N-I temperatures would be expected. However, the smectic phases of these compounds do not fall in thermal stability to such a marked degree, and as a result, these esters exhibit S-I transitions at fairly high temperatures. When n = 1 or 3, nematic properties therefore disappear, the thermal stability of the « N » phase falling below that of the S phase. As can be seen by reference to figure 2 or 3, an alternation between N-I and S-I transitions occurs on ascending the series.

Transitions involving smectic phases. — When n = 0 or 2, N and S phases are observed and when n = 1 or 3, only S phases are found; the number of S phases (Sx, Sb, Sb) depends largely on the ability of the systems to supercool.

The S phase exhibited by the 3'-chloro compound with n = 1 was identified, by its textural characteristics, as being a Sx phase, which on cooling only 1.7 °C changed its texture to that of a typical Sb phase. D. T. A. revealed a double peak, corresponding to the I-Sx and Sx-Sb transitions, on cooling the amorphous liquid and a further single peak at 127.1 °C, corresponding to a change from Sb-Sb. However, the S phase formed from the amorphous liquid of the 3'-methyl compound with n = 1 could not be identified by optical microscopic examination of its texture. D. T. A. showed only a single peak, on cooling from the amorphous liquid, before the peak occurred corresponding to the change to the Sb phase at 132.4 °C. In both these cases, the Sb phases could be identified by their textural characteristics.

When n = 2, N, Sx, Sb and Sb phases are found for the 3'-chloro compound; the Sx range is 24.9 °C and for the corresponding compound with n = 0 it is...
24.3 °C. Yet, as noted above, the $S_A$ range for the 3"-chloro ester with $n = 1$ is only 1.7 °C. It can be seen clearly from figure 2 that the thermal stabilities of the $S_A$ and $S_B$ phases alternate on passing from even to odd numbers of $-\text{CH}_2-$ units in the alkylene chain, and that the alternation is opposite in sense for $S_A$ and $S_B$ phases. The thermal stabilities of the $S_E$ phases also alternate, and the sense of alternation is the same as that for $S_B$. $S_A$ alternation is of the same sense as that for the $N$ thermal stability.

When $n = 3$, $S-I$ transitions are again found. The 3"-methyl compound exhibits a very short range (1.8 °C) $S_A$ phase, as well as $S_B$ and $S_E$ phases. The alternation in thermal stabilities can again be clearly seen in figure 3 and is much the same as that for the 3"-chloro compound. However, the 3"-chloro compound ($n = 3$) again produces an unusual $S$ texture on cooling from the amorphous liquid and this is similar to the $S$ texture exhibited by the 3"-methyl compound with $n = 1$. Examination by D. T. A. revealed similar features to those found for the 3"-methyl compound ($n = 1$).

The $S$ phases exhibited by the 3"-methyl compound with $n = 3$ were checked by miscibility with $n$-octyl 4-(4'-phenylbenzylideneamino) cinnamate which exhibits [5] $S_A$, $S_B$ and $S_E$ phases. The phase diagram (Fig. 4) shows that the phases exhibited by the 3"-methyl compound are $S_A$, $S_B$ and $S_E$.

![Phase diagram for n-octyl 4-(4'-phenylbenzylideneamino) cinnamate](image)

**Fig. 4.** — Phase diagram for n-octyl 4-(4'-phenylbenzylideneamino) cinnamate (A) with 3"-methyl-γ-phenylpropyl 4-(4'-phenylbenzylideneamino) cinnamate (B).

A very careful microscopic examination of the unique $S$ texture exhibited by the 3"-methyl compound ($n = 1$) and the 3"-chloro compound ($n = 3$) proved that there was no observable $S_A$-$S_B$ transition on cooling from the amorphous liquid before the $S_E$ phase formed. Also, no $S_B$-$S_A$ transition could be seen on a heating cycle from the $S_E$ phase to the amorphous liquid. Particular attention was paid to the formation of the $S$ phase from the amorphous liquid, because it was possible that a very short range $S_A$ phase might exist. However, no such feature was observed.

Plates 1 and 2 show the sequence of events on cooling the amorphous liquid of the 3"-methyl compound ($n = 1$) at temperatures of 169.9 °C and 167.0 °C, respectively.

It is noticeable that the individual fans are absolutely clear as soon as they form and that they do not change in this respect on further cooling. Plate 3 shows the $S_E$ phase formed by the same compound. The $S$ texture shown in Plate 2 is unique and is difficult to classify in terms of conventional textures, e.g., fan, mosaic,
etc. Areas of the texture appear almost fan-like, whereas others appear almost mosaic-like. Bearing in mind the clarity of the fans and the tendency to give a mosaic texture, the phase was tentatively classified as \( S_B \), especially as near neighbours in the homologous series exhibit \( S_A \) and \( S_B \) phases and the alternation in thermal stabilities is tending to extinguish the \( S_A \) phase.

Miscibility studies of the phases exhibited by the 3'-methyl compound \((n = 1)\) and the 3'-chloro compound \((n = 3)\) were carried out. Known weights of each component were mixed on a microscope slide and heated until the amorphous liquids formed. The components diffused together, a cover slip was placed on top of the preparation and the sample was viewed microscopically. Transition temperatures could then be measured [4] at accurately known percentage compositions.

The 3'-methyl compound \((n = 1)\) was mixed with \( n \)-octyl 4-(4'-phenylbenzyldieneamino) cinnamate [5] and the phase diagram is shown in figure 5. At 94%

\[
\text{FIG. 5. — Phase diagram for } n \text{-octyl 4-}(4' \text{-phenylbenzyldieneamino)} \text{ cinnamate (A) with 3'-(methylbenzyl4-)(4'-phenylbenzyldieneamino)} \text{ cinnamate (C).}
\]

of the 3'-methyl compound, a \( S_A-S_B \) transition was found 0.2 \( ^\circ \)C below the \( I-S_A \) transition; this transition involved typical transition bars and the appearance of textural cracks. However, at concentrations above 94\%, the texture formed from the amorphous liquid appeared exactly the same as that of the pure compound.

The 3'-chloro compound \((n = 3)\) behaved similarly; a \( S_A \) range of 0.2 \( ^\circ \)C was found at 95\% of the 3'-chloro compound.

The \( S_B \) phases of both the 3'-chloro and 3'-methyl compounds were separately completely miscible with the known \( S_B \) phase of the \( n \)-octyl ester.

Using a compound exhibiting \( N \) and \( S_A \) phases only \((2-(4'-n\text{-decyloxybenzyldieneamino)}) \text{ fluorene [6]})\), the phase diagram shown in figure 6 was obtained for the 3'-methyl compound \((n = 1)\). The \( N \) phase of the substituted fluorene is immiscible, but the \( S_A \) phase is miscible with the \( S \) phase of the 3'-methyl compound.

However, the region of miscibility narrows to a point at 100\% of the latter component. An \( S_A-S_B \) transition was found for compositions as high as 98\% of the 3'-methyl compound, at which composition the \( S_A \) range was 1.2 \( ^\circ \)C. The pure compound does not however show a \( S_A-S_B \) transition. The temperature range over which the \( S_A \) phase exists increases towards higher concentrations of the substituted fluorene and the \( S_B \) thermal stability falls. The \( S_E \) phase of the 3'-methyl compound is of course immiscible with any phase of the substituted fluorene.

A similar phase diagram was obtained for the 3'-chloro compound \((n = 3)\) on admixture with the substituted fluorene. Here, a \( S_A \) phase lasting over 1.8 \( ^\circ \)C was found at a composition of 97.5\% of the 3'-chloro compound.

It would seem that both \( S_A \) and \( S_B \) phases exist for the 3'-methyl compound \((n = 1)\) and 3'-chloro compound \((n = 3)\) but that their thermal stabilities coincide. When the thermal range of the \( S_A \) phase is selectively increased, by mixing with a compound exhibiting only a \( S_A \) modification, then a \( S_A-S_B \) transition soon occurs due to the relative decrease in \( S_B \) thermal stability. However, when both \( S_A \) and \( S_B \) thermal stabilities are maintained, the mixture behaves like the pure 3'-substituted compound until such a concentration that the \( S_A \) and \( S_B \) thermal stabilities become sufficiently different, and then a distinct \( S_A-S_B \) change occurs.

The \( S_A \) phase must therefore still exist; it does not become extinguished like the \( N \) phase. This suggests that it is necessary to form a transitional \( S_A \) phase intermediate between a \( S_B \) phase and the amorphous liquid, both on heating and cooling. If this were not so, the hexagonal ordering characteristic of \( S_B \) lamellae would have to exist as soon as the layers are produced on cooling from the amorphous liquid. For a \( I-S_B \) transition to occur, the molecules would presumably require to be already hexagonally packed in the pre-transitional smectic cycbotactic groups which probably
exist in the amorphous liquid just above the I-S transition. It would seem more probable however, that the molecules are randomly packed \( (S_A\) like) in these pretransitional groups. Moreover, if a heating cycle is considered, for a \( S_R \rightarrow I \) transition to occur, the molecules in the layers would have to remain hexagonally packed until the precise instant that the layers break up completely and form the amorphous liquid. The present evidence indicates that the layers first formed contain molecules which are arranged \textit{transitionally} in a random manner, \textit{before} they become hexagonally ordered. N-\( S_B \) transitions are known in a few cases \cite{7, 8, 9}; however, if the cooling process is considered, the molecules will already have one degree of order in this case in the preceding N phase, and the N-\( S_B \) change can be more readily envisaged.

These effects, were caused by the thermal stabilities of the \( S_A \) and \( S_B \) phases coinciding because of the different senses of alternation of the \( S_A \) and \( S_B \) thermal stabilities as the series were ascended. In view of this, it would probably be reasonable to designate this phase change as I-\( S_{AB} \), and thereby indicate that, although the phase is a \( S_B \) phase, its manner of formation is \textit{via} a transitional \( S_A \) phase: it is this feature which undoub-

tedly accounts for the unique texture, which we call a hybrid fan-mosaic texture \cite{1}.

These unique features are also found in the corresponding 4'-substituted \( \omega \)-phenylalkyl derivatives, but the compounds in these series crystallise more readily and the smectic phases are therefore more difficult to examine. The constants obtained for the 4'-methyl and 4'-chloro series are given in Table I and are shown graphically in figures 7 and 8. The same trends in meso-

![Figure 7](image7.png)

\textbf{FIG. 7.} — Plot of liquid crystal transition temperatures against \( n \), the number of methylene units in the alkylene chain for the 4'-methyl-\( \omega \)-phenylalkyl 4-(4'-phenylbenzyldieneamino) cinnamates

\textit{Key: } (\blacktriangle), N-I; (\blacklozenge), S_A-N; (\o), C-S_A, S_B, N or I; (\square), S_{AB-I}; (\bullet), S_B-S_B.

![Figure 8](image8.png)

\textbf{FIG. 8.} — Plot of liquid crystal transition temperatures against \( n \), the number of methylene units in the alkylene chain for the 4'-chloro-\( \omega \)-phenylalkyl 4-(4'-phenylbenzyldieneamino) cinnamates

\textit{Key: } (\blacktriangle), N-I; (\blacklozenge), S_A-N; (\o), C-S_B or N; (\square), S_{AB-I}; (\bullet), S_B-S_B.

phase thermal stability are found as for the 3'-substituted series and the \( S_{AB-I} \) transition, recognized solely by its textural characteristics, is found for all the compounds where \( n \) is odd. These two series, therefore

\( (1) \) The reader's attention is drawn to similar observations recently made by Billard on the compound 2,7-di-\( \pi \)-hexadecanoyl-fluorene \textit{(Proceedings of the Raman International Meeting on Liquid Crystals, Bangalore, December 1973, to be published)}. Billard has interpreted his observations in terms of a \textit{direct} I-\( S_B \) transition, and has pointed out to the authors that the texture of his \( S_B \) phase is closely similar to that shown in Plates 1 and 2 of the present paper.
provide good confirmatory evidence for the unique features observed for the 3'-substituted analogues.

The effects of 3'- and 4'-substituents on smectic thermal stabilities. — By reference to Table I, some observations may be made about the effects of 3'- and 4'-substituents (Me and Cl) on the thermal stabilities of the different smectic phases.

1. SMECTIC E. — The \( S_E \) thermal stabilities \((n = 1, 2 \text{ and } 3)\) are either decreased or increased by only a few \(^\circ\)C (largest increase = 6.1 \(^\circ\)C) by substitution in the ester phenyl ring. The substituents therefore play a relatively minor role in determining the thermal stability of this highly ordered \( S \) phase, and the dipole of the ring-\( \text{Cl} \) bond appears to be of no special importance.

2. SMECTIC B. — For the one even value of \( n \) for which comparisons can be made \((n = 2)\), 3'-Me and -\( \text{Cl} \) substituents decrease \( S_B \) thermal stability slightly, consistent with the breadth increases which the \( S_B \) substituents cause in the lath-like molecules. From molecular models, it appears that either spatial position in figure 1 broadens the system, and the two extreme possibilities are difficult to distinguish on this basis.

For \( n = 2 \), a 4'-Me substituent (terminal) causes a small decrease in \( S_B \) thermal stability. No comment can be made about the effect of a 4'-\( \text{Cl} \) substituent from the available results.

For odd \( n \) values, a comparison of \( S_B \) and \( S_A \) thermal stabilities of the possible packing arrangements of lath-like (left) and \( L \)-shaped (right) molecules in the presence of the terminal \( 3' \) and \( 4' \)-Me or \( \text{Cl} \) substituents shows that substitution in the ester phenyl ring causes a general, but quite small decrease in \( S_B \) thermal stability.

3. SMECTIC A. — For even values of \( n \), the terminal 4'-substituents diminish \( S_A \) thermal stability in the order \( H > \text{Me} \geq \text{Cl} \).

In this particular case, the terminal dipole of the 4'-\( \text{Cl} \) substituent appears to have an adverse effect on a \( S_A \) phase, as has been observed in some cases for terminal, polar groups like \( \text{CN} \) or \( \text{NO}_2 \) [10].

For \( n = 2 \), 3'-Me and -\( \text{Cl} \) substituents have similar small effects in decreasing \( S_A \) thermal stability, consistent with small breadth increases of the molecule. However, for \( n = 0 \), a 3'-Me substituent slightly increases \( S_A \) thermal stability, whereas a 3'-\( \text{Cl} \) substituent decreases it by 26.6 \(^\circ\)C. Both substituents are of similar size, and the dipolar 3'-\( \text{Cl} \) substituent causes the decrease.

Alternation of \( S_A \), \( S_B \), and \( S_E \) thermal stabilities. — As reported here and elsewhere [3], the thermal stabilities of \( N \) phases of phenyl and \( \omega \)-phenylalkyl esters alternate dramatically as \( n \) changes from even to odd and the molecular shape changes from lath-like to \( L \)-shaped. The situation is consistent with the much more open arrangement of \( L \)-shaped molecules (Fig. 9) which must exist in an \( N \) phase, to allow the translational and rotational freedom known to arise in this liquid crystal state.

However, \( S \) phases do not alternate nearly so dramatically in thermal stability (Fig. 2 and 3), and as a direct result, alternation between \( N-I \) and \( S-I \) transitions in such homologous series of \( \omega \)-phenylalkyl esters is common.

![Comparison of possible packings of lath-like (left) and L-shaped (right) molecules in nematic (top) and smectic (bottom) liquid crystals.](image_url)
The situation is that, as \( n \) changes from even to odd:

(a) \( S_a \) thermal stability decreases (as for \( N \) thermal stability), and

(b) \( S_h \) and \( S_e \) thermal stabilities increase.

In figure 9 are shown possible comparative packings of lath-like and L-shaped molecules in a smectic layer. In the case of the L-shaped molecules, no evidence for the actual ordering in the layers is available. However, besides polar order [11], two other types of order can be envisaged and these are shown. Neither involves a packing which is significantly different to the packing of lath-like molecules, but if some degree of rotational freedom of motion about the long axes is possible in \( S_a \) phases, the packing efficiency of L-shaped molecules would be less than that of lath-like molecules, and this would account for the trend in \( S_a \) thermal stability with change in \( n \). The lamellar packing is also much freer of motion about the long axes is much more reasonable that this may be the case in these more solid-like \( S \) phases, and should this be so, such that rotation is quenched or, at most, co-operative over substantial groups of molecules, a close packing of interlocked molecules over fairly extended groups may be envisaged for both \( S_h \) and \( S_e \) phases. It is conceivable that the nett interaction energy of stabilisation for such situations may be greater than for a packing of lath-like molecules, so accounting for the alternation trends for these two types of \( S \) phases.

Experimental section. — The synthesis of the Schiff's bases (Table I) began with the esterification of 4-nitrocinnamic acid with the methyl esters. 3- and 4-chlorophenylacetic acids were separately esterified using methanol and concentrated sulphuric acid. The liquid esters were obtained in good yields and mass spectrometry gave the correct molecular weights.

Substituted \( \beta \)-phenylethanol. — 3-methyl- and 4-chloro-\( \beta \)-phenylethanol were prepared by reduction of the esters with \( LiAlH_4 \) using a standard technique [14]. One reduction cycle produced an impure product in each case; the impurity was found, by infra-red spectroscopy, to be the original methyl ester. Two successive reductions gave the corresponding alcohols in good yields (ca. \( 60-75 \% \)) with purities of \( 97-99 \% \) by g. l. c. In each case the alcohol gave the required mass ion(s) by mass spectrometry.

Substituted \( \gamma \)-phenylpropanols. — 4-methyl-, 3-chloro- and 4-chloro-\( \gamma \)-phenylpropanols were synthesised from the commercially available, correspondingly substituted cinnamic acids. However, 3-methylcinnamic acid was prepared [15] from 3-methylbenzaldehyde and malonic acid. The yield was \( 52 \% \), m. p. 119-120° C (lit. m. p. 115° C [13]).

The substituted cinnamic acids were converted into the correspondingly substituted \( \beta \)-phenylpropionic acids by hydrogenation [4] using \( 10 \% \) Pd/C and hydrogen at 1 atmosphere pressure. Well stirred glacial acetic acid at 50° C was used as solvent. However, 4-chlorocinnamic acid is very insoluble in glacial acetic acid; it was therefore first esterified and the soluble methyl 4-chlorocinnamate, m. p. 81-82° C (Found: C, 61.0; H, 4.55; Cl, 17.8\% C\textsubscript{10}H\textsubscript{8}ClO\textsubscript{2} requires C, 61.2; H, 4.59; Cl, 18.12\%)

3-chloro-\( \beta \)-phenylpropionic acid, m. p. 65-66° C (lit. m. p. 77° C [13]), (Found: C, 58.3; H, 5.0; Cl, 18.7\% Calc. for C\textsubscript{9}H\textsubscript{8}ClO\textsubscript{2} C, 58.6; H, 4.9; Cl, 19.15\%)

Methyl 4-chloro-\( \beta \)-phenylpropionate, b. p. 82-84° C at 0.15 mm Hg.

Mass spectrometry gave the required mass ions (\( M = 200 \) and 198) in the expected isotopic ratio.

3-methyl-\( \beta \)-phenylpropionic acid, m. p. 45° C, b. p. 38° C at 0.2 mm Hg. (Found: C, 73.05; H, 7.45\% C\textsubscript{10}H\textsubscript{12}O\textsubscript{2} requires C, 73.2; H, 7.3\%)

4-methyl-\( \beta \)-phenylpropionic acid, m. p. 125-126° C (Found: C, 72.8; H, 7.4\% C\textsubscript{10}H\textsubscript{12}O\textsubscript{2} requires C, 73.2; H, 7.3\%)}
### Table II

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<td>3&quot;-Methylbenzyl</td>
<td>C_{17}H_{15}ClI_2O_4</td>
<td>69.5</td>
<td>5.5</td>
<td>4.5</td>
<td>-</td>
</tr>
<tr>
<td>4&quot;-Methylbenzyl</td>
<td>C_{18}H_{17}ClI_2O_4</td>
<td>62.9</td>
<td>4.6</td>
<td>4.0</td>
<td>10.3</td>
</tr>
<tr>
<td>3&quot;-Chloro-β-phenylethyl</td>
<td>C_{16}H_{16}ClI_2O_4</td>
<td>70.2</td>
<td>5.9</td>
<td>4.3</td>
<td>-</td>
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<tr>
<td>4&quot;-Chloro-β-phenylethyl</td>
<td>C_{19}H_{19}ClI_2O_4</td>
<td>76.4</td>
<td>6.4</td>
<td>5.2</td>
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</tr>
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</table>

### Table III

<table>
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<tr>
<th>Ester group</th>
<th>Formula</th>
<th>Required</th>
<th>Analysis</th>
<th>Found</th>
<th>n.p. (°C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>Cl</td>
</tr>
<tr>
<td>3&quot;-Chlorophenyl</td>
<td>C_{15}H_{12}ClI_2O_2</td>
<td>65.8</td>
<td>4.4</td>
<td>5.1</td>
<td>13.0</td>
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<tr>
<td>4&quot;-Chlorophenyl</td>
<td>C_{16}H_{17}ClI_2O_2</td>
<td>75.8</td>
<td>5.9</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>3&quot;-Methylphenyl</td>
<td>C_{16}H_{15}ClI_2O_2</td>
<td>66.9</td>
<td>5.0</td>
<td>4.7</td>
<td>12.5</td>
</tr>
<tr>
<td>4&quot;-Methylphenyl</td>
<td>C_{17}H_{17}ClI_2O_2</td>
<td>76.3</td>
<td>6.5</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>3&quot;-Chloro-β-phenylethyl</td>
<td>C_{17}H_{16}ClI_2O_2</td>
<td>67.7</td>
<td>5.3</td>
<td>4.6</td>
<td>11.8</td>
</tr>
<tr>
<td>4&quot;-Chloro-β-phenylethyl</td>
<td>C_{18}H_{17}ClI_2O_2</td>
<td>76.9</td>
<td>6.8</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>3&quot;-Methyl-β-phenylethyl</td>
<td>C_{16}H_{15}ClI_2O_2</td>
<td>69.5</td>
<td>5.7</td>
<td>4.4</td>
<td>11.3</td>
</tr>
<tr>
<td>4&quot;-Methyl-β-phenylethyl</td>
<td>C_{19}H_{21}ClI_2O_2</td>
<td>71.6</td>
<td>7.1</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>3&quot;-Chloro-γ-phenylpropyl</td>
<td>C_{19}H_{21}ClI_2O_2</td>
<td>77.6</td>
<td>7.3</td>
<td>4.4</td>
<td>-</td>
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</tbody>
</table>
The three acids above (and 4-chlorocinnamic acid) were esterified using methanol and concentrated sulphuric acid. In each case, where the methyl ester was an oil, mass spectrometry gave the required mass ion(s).

Methyl 4-methyl-\(\beta\)-phenypropionate  
\[\text{b. p. 82-84 } ^\circ\text{C at 0.2 mm Hg.}\]

Methyl 3-methyl-\(\beta\)-phenypropionate  
\[\text{b. p. 88-90 } ^\circ\text{C at 0.55 mm Hg.}\]

Methyl 3-chloro-\(\beta\)-phenypropionate  
\[\text{b. p. 120 } ^\circ\text{C at 2.0 mm Hg.}\]

The four esters were separately reduced [14] using LiAlH\(_4\); the products after one reduction cycle were 95-99\% pure by g.l.c.

In each case the alcohols gave the required mass ions by mass spectrometry.

4-methyl-\(\gamma\)-phenylpropanol  
\[\text{b. p. 108 } ^\circ\text{C at 1.1 mm Hg.}\]

3-methyl-\(\gamma\)-phenylpropanol  
\[\text{b. p. 94-96 } ^\circ\text{C at 0.3 mm Hg.}\]

4-chloro-\(\gamma\)-phenylpropanol  
\[\text{b. p. 102 } ^\circ\text{C at 0.15 mm Hg.}\]

3-chloro-\(\gamma\)-phenylpropanol  
\[\text{b. p. 128-132 } ^\circ\text{C at 2.8 mm Hg.}\]

Substituted phenyl and \(\omega\)-phenylalkyl 4-nitro- and \(-\)amino-cinnamates. — These were prepared via 4-nitrocinamoyl chloride [16] by interaction [5] with the alcohol (or phenol) in pyridine as solvent. The esters, which were all solids, were purified by crystallisation from light petroleum (b.p. 40-60 °C) and toluene. Each ester moved as a single spot on thin layer chromatography. The melting points and elemental analysis results are given in Table II.

The amino-esters were prepared by reduction of the nitro-esters by heating with iron pin dust in a mixture of 20% aqueous acetic acid and ethanol following the procedure of Semonsky and Kunak [17]. The products were purified and crystallised from light petroleum (b.p. 40-60 °C) and toluene. The melting points and elemental analysis results are given in Table III.

Schiff’s bases. — The pure amino-esters (1 mol) were interacted separately with biphenyl-4-carboxaldehyde (1.1 mol) using as solvent boiling ethanol containing a trace of acetic acid as catalyst and a reaction time of 20 min. The Schiff’s bases were crystallised until their m. p. s. and liquid crystal transition temperatures were constant; the solvents used were ethanol and a mixture of light petroleum (b.p. 40-60 °C) and toluene. The constants for these compounds, which were obtained using a Nikon polarising microscope and a Mettler FP52 hot stage, are given in Table I and the elemental analysis results in Table IV.

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References