NOVEL SMECTIC POLYMORPHIC BEHAVIOUR IN HOMOLOGOUS SERIES OF MESOGENS

D. Coates, G. Gray

To cite this version:

D. Coates, G. Gray. NOVEL SMECTIC POLYMORPHIC BEHAVIOUR IN HOMOLOGOUS SERIES OF MESOGENS. Journal de Physique Colloques, 1975, 36 (C1), pp.C1-365-C1-374. <10.1051/jphyscol:1975160>. <jpa-00216239>

HAL Id: jpa-00216239
https://hal.archives-ouvertes.fr/jpa-00216239
Submitted on 1 Jan 1975

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
NOVEL SMECTIC POLYMORPHIC BEHAVIOUR
IN HOMOLOGOUS SERIES OF MESOGENS

D. COATES and G. W. GRAY

Department of Chemistry, University of Hull, Hull, HU6 7RX, England

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 alkyene 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 SA-SA transition could be detected microscopically or by D. T. A., miscibility studies indicated that a transitional SA phase still existed. This suggests that it is necessary to form a transitional SA phase intermediate between the amorphous liquid and a SA phase, both on heating and cooling. This transition has been called SAB-I.

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

The relative effects of 3'- and 4'-methyl- and chloro-substituents on N, SA, SB and SE thermal stabilities are discussed.

Introduction. Several series of phenyl and \( \omega \)-phenylalkyl 4-(4'-substituted benzylideneamino) cinnamates (I) were studied by Gray and Harrison [1, 2] and very large alternations in nematic (N)

\[
\begin{align*}
X &\equiv \underbrace{\text{CH\equivN\equivCH=CHCOO(CH}_{2})_{n}\equiv
\end{align*}
\]

thermal stabilities were found as the value of \( n \), the number of methylene units in the alkyene chain, changed from even to odd (from 0 to 4). These very high alternations in N thermal stability, compared, for example, with the alternations in N-I transition temperatures normally found for homologous series of
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 molecules, 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), a phenyl group, smectic polymorphism occurred. The thermal stabilities of both smectic A (S\textsubscript{A}) and smectic B (S\textsubscript{B}) phases also alternated, but to a much smaller extent; the alternations of the transition temperatures S\textsubscript{A}-N or I and S\textsubscript{B}-S\textsubscript{A} were in fact of opposite senses. These smaller alternations were also accounted for in terms of molecular shape. Smectic E (S\textsubscript{E}) phases were commonly exhibited on cooling the S\textsubscript{B} 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 CH\textsubscript{3}-Ph (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'-phenylbenzylideneamino) 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 S\textsubscript{E} phase are listed. These unsubstituted homologues exhibit at the most S\textsubscript{A} - N-I transition temperatures, 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-\( \omega \)-phenylalkyl 4-(4'-phenylbenzylideneamino) cinna-mates

Key: \( (\Delta) \), N-I; \( (\triangle) \), S\(_{A}\)-I or N; \( (\bigcirc) \), C-S\(_{A}\), S\(_{B}\) or I; \( (\square) \), S\(_{AB}\)-I; \( (\bullet) \), S\(_{B}\)-S\(_{A}\); \( (\bullet\bullet) \), S\(_{B}\)-S\(_{B}\).

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 (S\(_{A}\), S\(_{B}\), S\(_{E}\)) 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 S\(_{A}\) phase, which on cooling only 1.7 °C changed its texture to that of a typical S\(_{B}\) phase. D. T. A. revealed a double peak, corresponding to the I-S\(_{A}\) and S\(_{A}\)-S\(_{B}\) transitions, on cooling the amorphous liquid and a further single peak at 127.1 °C, corresponding to a change from S\(_{B}\)-S\(_{E}\). 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 S\(_{E}\) phase at 132.4 °C. In both these cases, the S\(_{B}\) phases could be identified by their textural characteristics.

When \( n = 2 \), N, S\(_{A}\), S\(_{B}\) and S\(_{E}\) phases are found for the 3'-chloro compound; the S\(_{A}\) 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 --CH$_2$-- units in the alkylen 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 $S_E$.

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'-phenylbenzylideneamino) cinnamate and the phase diagram is shown in figure 5. At 94% of the 3"-methyl compound, a $S_A-S_B$ transition was found for compositions as high as 98% of the 3"-methyl compound, at which composition the $S_A$ range was 1.2 °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 $S_B$ 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 °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

![Figure 6. Phase diagram for 2-(4'-n-decyloxybenzylideneamino) fluorene (D) with 3"-methylbenzyl 4-(4'-phenylbenzylideneamino) cinnamate (C).](image-url)
exist in the amorphous liquid just above the I-S transition. It would seem more probable however, that the molecules are randomly packed (Sₐ like) in these pretransitional groups. Moreover, if a heating cycle is considered, for a Sₖ-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 transitonally in a random manner, before they become hexagonally ordered. N-Sₖ transitions are known in a few cases [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-Sₖ change can be more readily envisaged.

These effects, were caused by the thermal stabilities of the Sₐ and Sₖ phases coinciding because of the different senses of alternation of the Sₐ and Sₖ thermal stabilities as the series were ascended. In view of this, it would probably be reasonable to designate this phase change as I-Sₖ₋ₐ and thereby indicate that, although the phase is a Sₖ phase, its manner of formation is via a transitional Sₐ phase: it is this feature which undoub-

![Diagram of liquid crystal transition temperatures against n] Fig. 7. — Plot of liquid crystal transition temperatures against n, the number of methylene units in the alkylene chain for the 4'-methyl-ω-phenylalkyl 4-(4'-phenylbenzylideneamino) cinna-
mates

Key: (▲), N-I; (△), S₆-N; (○), C-Sₖ, Sₐ, N or I; (□), Sₖ-I; (●), Sₐ-Sₖ.

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

![Diagram of liquid crystal transition temperatures against n] Fig. 8. — Plot of liquid crystal transition temperatures against n, the number of methylene units in the alkylene chain for the 4''-chloro-ω-phenylalkyl 4-(4'-phenylbenzylideneamino) cinna-
mates

Key: (▲), N-I; (△), S₆-N; (○), C-Sₖ or N; (□), Sₖ-I; (●), Sₐ-Sₖ.

(1) The reader's attention is drawn to similar observations recently made by Billard on the compound 2,7-di-n-hexadecanoylfluorene (Proceedings of the Raman International Meeting on Liquid Crystals, Bangalore, December 1973, to be published). Billard has interpreted his observations in terms of a direct I-Sₖ transition, and has pointed out to the authors that the texture of his Sₖ phase is closely similar to that shown in Plates 1 and 2 of the present paper.
provides 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 ($n = 1, 2$ and $3$) are either decreased or increased by only a few $°C$ (largest increase = $6.1 °C$) 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-$Cl$ 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 -Cl substituents decrease $S_B$ thermal stability slightly, consistent with the breadth increases which the lateral 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'-Cl substituent from the available results.

For odd $n$ values, a comparison of $S_B$-$S_A$ and $S_{AB}$-$I$ temperatures shows that substitution in the ester phenyl ring causes general, but quite small decreases (largest decrease = $ca. 10 °C$) in $S_B$ thermal stability. For 4'-substituents, the effect is presumably due to an increase in breadth of the L-shaped molecule. This may also be true for 3'-substituents, but on the available evidence, the two extreme spatial positions shown in figure 1 cannot again be distinguished. One position is lateral and breadth increasing, and the other is terminal, but, as has been noted above for $n = 2$, a terminal 4''-Me substituent itself diminishes $S_B$ thermal stability.

3. SMECTIC A. — For even values of $n$, the terminal 4'-substituents diminish $S_A$ thermal stability in the order $H > Me > Cl$.

In this particular case, the terminal dipole of the 4''-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 CN or NO$_2$ [10].

For $n = 2$, 3''-Me and -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''-Cl substituent decreases it by $26.6 °C$. Both substituents are of similar size, and the dipolar 3''-Cl substituent causes the decrease; it would appear that the effect may be dipolar in nature, e.g., intermolecular repulsive interactions between ring-$Cl$ and C=O dipoles of neighbouring molecules which are in close proximity when $n = 0$. The increase in $S_A$ thermal stability for the 3''-Me derivative is however interesting, and it is possible that the ring-Me and C=O dipoles of neighbouring molecules slightly reinforce each other and cause an attraction. It is also possible however that the effects of 3''-substituents in the two extreme spatial positions indicated in figure 1 are more different than molecular models suggest they will be. The results may therefore indicate that different conformations are adopted by the two 3''-substituted esters, because of restricted rotation about the O-ring bond.

For odd values of $n$, 3''- and 4'-substituents diminish $S_A$ thermal stability consistently; the largest effect is $13.1 °C$ and the situation is comparable with that for $S_B$ phases.

Although no clear cut picture emerges concerning the relative effects of 3''- and 4'-Me and -Cl substituents on the different $S$ phases, it is valuable to recognize the variable effects which do arise, since they serve to warn against generalising too readily about the role of substituents in such systems.

Alteration 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 w-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 w-phenylalkyl esters is common.
The situation is that, as \( n \) changes from even to odd:
(a) \( S_\alpha \) thermal stability decreases (as for \( N \) thermal stability), and
(b) \( S_\beta \) and \( S_\delta \) 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 \( S_\alpha \) 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 \( S_\alpha \) thermal stability with change in \( n \). The lamellar packing is also much closer than that for L-shaped molecules in the N phase (Fig. 9), and the fact that the thermal stability of the S phase exceeds that of the N phase for odd values of \( n \), giving direct S-I changes, may be explained.

Finally, an explanation is required for the increase in \( S_\beta \) thermal stability which accompanies the change from even to odd \( n \) values and gives rise to \( S_{AB} \) changes. That is, why should non-lath-like molecules favour \( S_\beta \) (and also \( S_\delta \)) phases? It is difficult to explain this, unless it is assumed that, at least for these molecular systems, rotational freedom about the molecular long axes is much less than in \( S_\alpha \) phases. It is not unreasonable 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 \( S_\beta \) and \( S_\delta \) phases. It is conceivable that the net 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 (via the acid chloride) with the appropriate substituted phenols or \( \alpha \)-phenylalkanols. The 3- and 4-methyl- and -chloro-phenols and -benzyl alcohols were commercially available. However, the substituted \( \beta \)-phenylethanalns and \( \gamma \)-phenylpropanols were synthesised.

The nitro-esters were reduced by iron and acetic acid to the corresponding amino-esters which were condensed with diphenyl-4-carboxaldehyde to form the Schiff's bases.

**Substituted \( \beta \)-phenylethanals.** — These were prepared from the correspondingly substituted phenylacetic acids via the methyl esters. 3- and 4-chlorophenylacetic acids were commercially available.

3- and 4-methylphenylacetic acids were synthesised from 3- and 4-methylbenzyl bromides by carboxylation of the Grignard reagents [12], followed by acidification: m. p. of the 3-isomer, 59-60°C (lit. m. p. 61°C [13]); m. p. of the 4-isomer, 92-93°C (lit. m. p. 91-92°C [13]).

The four 3- and 4-methyl- and -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.

The four substituted \( \beta \)-phenylethanals 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.

- 3-chloro-\( \beta \)-phenylethanol
  - b. p. 73-75°C at 0.02 mm Hg.
- 4-chloro-\( \beta \)-phenylethanol
  - b. p. 79-84°C at 0.03 mm Hg.
- 3-methyl-\( \beta \)-phenylethanol
  - b. p. 61-62°C at 0.2 mm Hg.
- 4-methyl-\( \beta \)-phenylethanol
  - b. p. 86°C at 0.8 mm Hg.

**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 sterilised 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%; \( C_{10}H_{8}ClO_2 \) requires C, 61.2; H, 4.59; Cl, 18.12%). It was hydrogenated.

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 \( C_7H_5ClO_2 \); 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%; \( C_{10}H_{12}O_2 \) requires C, 73.2; H, 7.3%).

4-methyl-\( \beta \)-phenylpropionic acid, m. p. 125-126°C (Found: C, 72.8; H, 7.4%; \( C_{10}H_{12}O_2 \) requires C, 73.2; H, 7.3%).
## Table II

<table>
<thead>
<tr>
<th>Ester Group</th>
<th>Hol. Formula</th>
<th>Required</th>
<th>Analysis</th>
<th>Found</th>
<th>n.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N</td>
<td>Cl</td>
<td>C  H  N</td>
<td>Cl</td>
</tr>
<tr>
<td>3'-Chlorophenyl</td>
<td>C₁₅H₁₉Cl₂O₂₄</td>
<td>60.1 3.3 4.7</td>
<td>11.0</td>
<td>59.8 3.2 4.7</td>
<td>11.6</td>
</tr>
<tr>
<td>4'-Chlorophenyl</td>
<td></td>
<td>59.8 3.4 4.7</td>
<td>12.0</td>
<td>59.8 3.4 4.7</td>
<td>12.0</td>
</tr>
<tr>
<td>3'-Methylphenyl</td>
<td>C₁₆H₁₅Cl₂O₂₄</td>
<td>67.8 4.6 4.9</td>
<td>-</td>
<td>67.5 4.5 5.0</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methylphenyl</td>
<td></td>
<td>67.8 4.6 4.9</td>
<td>-</td>
<td>67.8 4.6 4.9</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chlorobenzyl</td>
<td>C₁₆H₁₂Cl₁₀O₂₄</td>
<td>60.5 3.0 4.4</td>
<td>11.2</td>
<td>60.6 4.1 4.3</td>
<td>11.3</td>
</tr>
<tr>
<td>4'-Chlorobenzyl</td>
<td></td>
<td>60.6 3.8 4.2</td>
<td>11.2</td>
<td>60.6 3.8 4.2</td>
<td>11.2</td>
</tr>
<tr>
<td>3'-Ethylbenzyl</td>
<td>C₁₇H₁₅Cl₂O₂₄</td>
<td>60.7 5.0 4.7</td>
<td>-</td>
<td>60.7 5.1 4.5</td>
<td>-</td>
</tr>
<tr>
<td>4'-Ethylbenzyl</td>
<td></td>
<td>60.4 5.0 4.6</td>
<td>-</td>
<td>60.4 5.0 4.6</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chloro-β-phenylethyl</td>
<td>C₁₇H₁₄Cl₂O₂₄</td>
<td>61.5 4.2 4.2</td>
<td>10.7</td>
<td>61.3 4.1 4.3</td>
<td>10.9</td>
</tr>
<tr>
<td>4'-Chloro-β-phenylethyl</td>
<td></td>
<td>61.5 4.2 4.3</td>
<td>10.9</td>
<td>61.5 4.2 4.3</td>
<td>10.9</td>
</tr>
<tr>
<td>3'-Methyl-β-phenylethyl</td>
<td>C₁₈H₁₄Cl₂O₂₄</td>
<td>69.5 5.5 4.5</td>
<td>-</td>
<td>69.4 5.5 4.6</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methyl-β-phenylethyl</td>
<td></td>
<td>69.5 5.5 4.6</td>
<td>-</td>
<td>69.5 5.5 4.6</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chloro-γ-phenylpropyl</td>
<td>C₁₇H₁₆Cl₂O₂₄</td>
<td>62.5 4.6 4.0</td>
<td>10.3</td>
<td>62.9 4.7 4.0</td>
<td>10.4</td>
</tr>
<tr>
<td>4'-Chloro-γ-phenylpropyl</td>
<td></td>
<td>62.7 4.6 4.1</td>
<td>10.2</td>
<td>62.7 4.6 4.1</td>
<td>10.2</td>
</tr>
<tr>
<td>3'-Methyl-γ-phenylpropyl</td>
<td>C₁₉H₁₉Cl₂O₂₄</td>
<td>70.2 5.9 4.5</td>
<td>-</td>
<td>70.3 6.1 4.2</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methyl-γ-phenylpropyl</td>
<td></td>
<td>70.1 5.9 4.3</td>
<td>-</td>
<td>70.1 5.9 4.3</td>
<td>-</td>
</tr>
</tbody>
</table>

## Table III

<table>
<thead>
<tr>
<th>Ester Group</th>
<th>Hol. Formula</th>
<th>Required</th>
<th>Analysis</th>
<th>Found</th>
<th>n.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N</td>
<td>Cl</td>
<td>C  H  N</td>
<td>Cl</td>
</tr>
<tr>
<td>3'-Chlorophenyl</td>
<td>C₁₅H₁₂Cl₂O₂₄</td>
<td>65.8 4.4 5.1</td>
<td>13.0</td>
<td>65.5 4.3 5.1</td>
<td>12.7</td>
</tr>
<tr>
<td>4'-Chlorophenyl</td>
<td></td>
<td>65.8 4.4 5.2</td>
<td>12.8</td>
<td>65.8 4.4 5.2</td>
<td>12.8</td>
</tr>
<tr>
<td>3'-Methylphenyl</td>
<td>C₁₆H₁₅Cl₂O₂₄</td>
<td>75.8 5.9 5.5</td>
<td>-</td>
<td>75.8 5.9 5.5</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methylphenyl</td>
<td></td>
<td>76.0 6.0 5.4</td>
<td>-</td>
<td>76.0 6.0 5.4</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chlorobenzyl</td>
<td>C₁₆H₁₄Cl₂O₂₄</td>
<td>66.6 4.9 4.9</td>
<td>12.3</td>
<td>66.9 5.0 4.7</td>
<td>12.5</td>
</tr>
<tr>
<td>4'-Chlorobenzyl</td>
<td></td>
<td>67.1 5.0 4.9</td>
<td>12.4</td>
<td>67.1 5.0 4.9</td>
<td>12.4</td>
</tr>
<tr>
<td>3'-Ethylbenzyl</td>
<td>C₁₇H₁₇Cl₂O₂₄</td>
<td>76.4 6.4 5.2</td>
<td>-</td>
<td>76.5 6.5 5.0</td>
<td>-</td>
</tr>
<tr>
<td>4'-Ethylbenzyl</td>
<td></td>
<td>76.5 6.5 5.1</td>
<td>-</td>
<td>76.5 6.5 5.1</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chloro-β-phenylethyl</td>
<td>C₁₇H₁₆Cl₂O₂₄</td>
<td>67.7 5.3 4.6</td>
<td>11.8</td>
<td>67.6 5.2 5.0</td>
<td>11.8</td>
</tr>
<tr>
<td>4'-Chloro-β-phenylethyl</td>
<td></td>
<td>67.6 5.2 4.8</td>
<td>12.0</td>
<td>67.6 5.2 4.8</td>
<td>12.0</td>
</tr>
<tr>
<td>3'-Methyl-β-phenylethyl</td>
<td>C₁₈H₁₅Cl₂O₂₄</td>
<td>76.9 6.8 5.0</td>
<td>-</td>
<td>76.9 6.7 4.9</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methyl-β-phenylethyl</td>
<td></td>
<td>77.2 6.8 4.7</td>
<td>-</td>
<td>77.2 6.8 4.7</td>
<td>-</td>
</tr>
<tr>
<td>3'-Chloro-γ-phenylpropyl</td>
<td>C₁₉H₁₈Cl₂O₂₄</td>
<td>63.5 5.7 4.4</td>
<td>11.3</td>
<td>63.4 5.7 4.4</td>
<td>11.0</td>
</tr>
<tr>
<td>4'-Chloro-γ-phenylpropyl</td>
<td></td>
<td>63.2 5.7 4.4</td>
<td>10.9</td>
<td>63.2 5.7 4.4</td>
<td>10.9</td>
</tr>
<tr>
<td>3'-Methyl-γ-phenylpropyl</td>
<td>C₁₉H₂₁Cl₂O₂₄</td>
<td>77.6 7.1 4.7</td>
<td>-</td>
<td>77.6 7.3 4.4</td>
<td>-</td>
</tr>
<tr>
<td>4'-Methyl-γ-phenylpropyl</td>
<td></td>
<td>77.2 7.1 4.6</td>
<td>-</td>
<td>77.2 7.1 4.6</td>
<td>-</td>
</tr>
</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-β-phenylpropionate
b. p. 82-84 °C at 0.2 mm Hg.

Methyl 3-methyl-β-phenylpropionate
b. p. 95-99 °C at 0.55 mm Hg.

Methyl 3-chloro-β-phenylpropionate
b. p. 120 °C at 2.0 mm Hg.

The four esters were separately reduced [14] using LiAlH₄; 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-γ-phenylpropanol
b. p. 108 °C at 1.1 mm Hg.

3-methyl-γ-phenylpropanol
b. p. 94-96 °C at 0.3 mm Hg.

4-chloro-γ-phenylpropanol
b. p. 102 °C at 0.15 mm Hg.

3-chloro-γ-phenylpropanol
b. p. 128-132 °C at 2.8 mm Hg.

The products after one reduction cycle 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.

The amino-esters were prepared 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.

<table>
<thead>
<tr>
<th>Table IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester group</td>
</tr>
<tr>
<td>Chlorophenyl</td>
</tr>
<tr>
<td>Chloropropionate</td>
</tr>
<tr>
<td>Methylpropionate</td>
</tr>
<tr>
<td>N-Methylacetamide</td>
</tr>
<tr>
<td>Chloroacetyl</td>
</tr>
<tr>
<td>Chloroacetamide</td>
</tr>
</tbody>
</table>

Acknowledgment. — The authors acknowledge with gratitude a maintenance grant (to D. C.) from the Science Research Council, London.

References