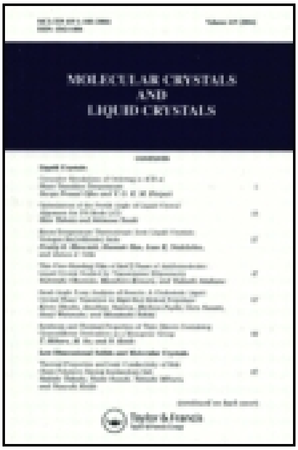

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Studies of Mesophase Transformations for Certain Schiff's Base Esters†

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Abstract—Schiff's bases derived from esters of *p*-aminocinnamic acid continue to be of interest because of novel mesophase transformations that they exhibit.

At Berlin, preliminary results for the homologous methyl to *n*-decyl 4-(*p*-phenylbenzylideneamino)cinnamates were described which indicated that smectic polymorphism was important in the series. Results of differential thermal analysis, optical microscopy and miscibility studies now presented show that most of the homologues give a smectic *A*, a smectic *B* and an uncharacterized smectic 3 phase. Regular changes in smectic–smectic transition temperatures occur along the series. Photomicrographs reveal differences in the fan and other textures of the three smectic phases, particularly for smectic 3, a tentative structure and assignment for which are discussed.

Studies of di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate have shown that the " focal-conic " or plane texture of the cholesteric phase undergoes three reversible transformations in forming the amorphous liquid. Photographic evidence for these changes is presented and discussed. Following these observations, cholesteric to amorphous liquid transformations for two other types of cholesterogen (cholesteryl esters and (-)2-methylbutyl 4-(*p*-substituted-benzylideneamino)cinnamates) have been re-examined. Results are presented showing that the cholesteric mesophases of the three types of cholesterogen change to the amorphous liquid on heating and reform from the liquid on cooling in significantly different ways.

1. Introduction

Although Schiff's bases derived from esters of *p*-aminocinnamic acid and *p*-aminobenzoic acid were amongst the earliest mesogens prepared, their study continues to reveal new features of interest, with particular regard to novel mesophase transformations.

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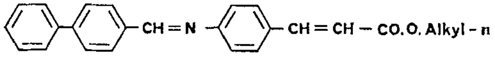
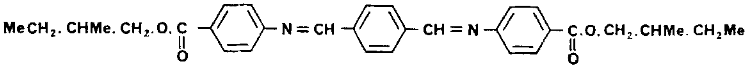
† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

The work reported is concerned primarily with three systems:

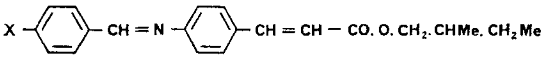
1. *n*-Alkyl 4-(*p*-phenylbenzylideneamino)cinnamates
   (Alkyl= methyl—*n*-decyl)



2 Di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate
(and the racemic modification)



3. (-)2-Methylbutyl 4-(*p*-substituted-benzylideneamino)cinnamates



where X = CN, NO_2, Cl, OMe

2. Results and Discussion

1. METHYL TO *n*-DECYL 4-(*p*-PHENYLBENZYLIDENEAMINO)CINNAMATES

Preliminary results for this homologous series were reported(1) after the compounds had been examined by optical microscopy and the transition temperatures determined by the capillary method. The plot of these temperatures against the number of methylene groups in the *n*-alkyl chain is given in Fig. 1; there was considerable dubiety about the region denoted S_2(?). Optical microscopy revealed no well defined changes on heating the crystalline solids until either the nematic or the amorphous liquids were formed. By the capillary method, sudden shrinking was, however, noted at the temperatures denoted by open circles; on further heating, softening or smearing occurred in many cases, but no definite changes were seen until typical smectic fluids formed at the temperatures denoted by closed circles. D.T.A. of the ethyl ester gave four transitions on heating, corresponding to those indicated by the capillary method, and three of these (N–I, S_1–N and S_2(?)–S_1) were precisely reversible on cooling. This suggested that S_2(?) was indeed a smectic phase, and that the series exhibited smectic polymorphism.

The entire series has now been examined by D.T.A. and Fig. 2 presents a plot of the transition temperatures against number of

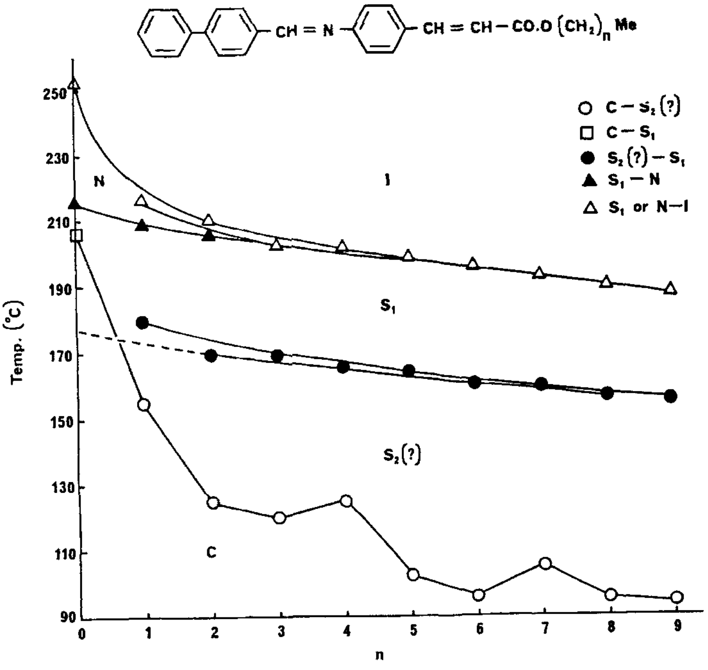


Figure 1. Plot of transition temperatures, determined by the capillary method, against the number of methylene units in the *n*-alkyl chain for the *n*-alkyl 4-(*p*-phenylbenzylideneamino)cinnamates.

methylene groups in the alkyl chain. Three smectic phases occur for most of the esters. The most thermally stable of these, S_1 in Fig. 1, is now denoted by S_A, since the phase is miscible in all proportions with the known smectic *A* phase of *n*-butyl 4-(*p*-methoxybenzylideneamino)cinnamate.⁽²⁾ Cooling S_A gives S_B, formerly denoted by S_2(?), and miscibility studies using the known smectic *B* phase of the above *n*-butyl ester confirm that it is of the *B* type. The S_B–S_A

transitions are precisely reversible, and the transitions temperatures alternate regularly along the series, but in the reverse manner to that for the S_A–I transitions.

For the ethyl to *n*-decyl esters, a precisely reversible transition involving a third smectic phase (S_3) occurs at the temperatures

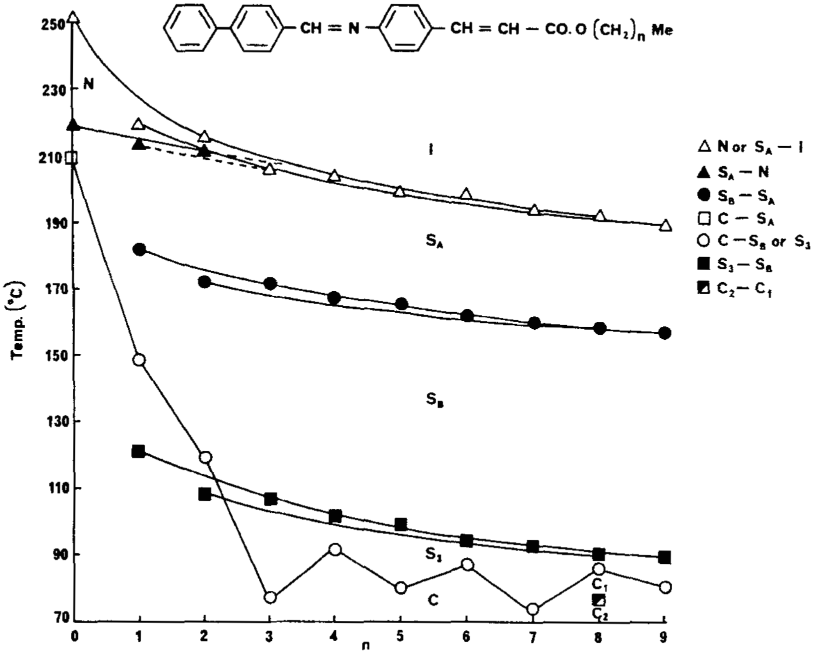


Figure 2. Plot of transition temperatures, determined by differential thermal analysis, against the number of methylene units in the *n*-alkyl chain for the *n*-alkyl 4-(*p*-phenylbenzylideneamino)cinnamates.

represented by closed squares; for the ethyl and *n*-propyl esters, the changes are monotropic. Allowing for differences between transition temperatures measured by D.T.A.—see Table 1—and the capillary method,⁽¹⁾ it is clear that the temperatures denoted by open circles (Fig. 1) approximated in some cases to those for S_3–S_B changes, but in others were higher than these transition temperatures, i.e., both C–S_3 and S_3–S_B changes occurred undetected. For the ethyl and *n*-propyl esters, the temperatures denoted by open circles

TABLE 1 Temperatures (T), enthalpies (ΔH) and entropies (ΔS) of transition for n-Alkyl 4-(p-phenylbenzylideneamino)cinnamates[d]

Alkyl	C–S_A, S_B or S_3			S_3–S_B			S_B–S_A			S_A–N			N or S_A–I		
	T^a	ΔH^a	ΔS^a	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	
Methyl	209	6.51	13.5	—	—	—	—	—	—	219	0.72	1.46	252	0.08	0.15
Ethyl	148	4.23	10.0	[121	0.27	0.70][b]	182	0.81	1.78	213	0.93	1.92	219	0.04	0.08
Propyl	119	5.08	13.0	[108	0.24	0.63]	172	0.76	1.71	211	0.84	1.74	215	0.08	0.16
Butyl	77	4.42	12.6	107	0.22	0.58	172	0.78	1.75	—	—	—	206	1.14	2.38
Pentyl	92	6.35	17.4	101.5	0.15	0.40	168	0.76	1.73	—	—	—	204	1.12	2.35
Hexyl	80	5.07	14.4	99	0.12	0.32	165.5	0.85	1.93	—	—	—	199	1.15	2.44
Heptyl	87	6.17	17.1	94	0.20	0.55	162	0.68	1.56	—	—	—	198	1.18	2.51
Octyl	73	9.44	27.3	93	0.16	0.44	160	0.62	1.43	—	—	—	194	1.11	2.38
Nonyl[c]	86	9.83	27.6	90	0.15	0.41	158	0.66	1.53	—	—	—	192	1.22	2.62
Decyl	80	8.30	23.5	90	0.10	0.27	157	0.85	1.96	—	—	—	189	1.25	2.71

[ ] Monotropic transition.

[a] T (°C); ΔH (kcal mol^{-1}); ΔS (cal mol^{-1} °K^{-1})—all measured by D.T.A.

[b] Data obtained only from a cooling cycle.

[c] Dimorphic C_2–C_1, 77°; ΔH, 2.40; ΔS, 6.86.
C_1–S_3, 86°; ΔH, 7.43; ΔS, 20.7.

[d] Three of these esters have been reported previously:
1. Methyl: C–S, 208 °C; S–N, 220 °C; N–I, 256 °C (Kasten, W., *Dissertation*, *Halle* (1909)).
2. Ethyl: C–S_B, 143.3 °C; S_B–S_A, 181.9 °C; S_A–N, 211.2 °C; N–I, 217 °C (Demus, D. and Sackmann, H., *Z. Phys. Chem.* (Leipzig) **238**, 215 (1968)).
3. Butyl: C–S, 167 °C; S–I, 203 °C (Vorländer, D., *Z. Phys. Chem.* (Leipzig) **57**, 357 (1907)).

approximated to those for the C–S_B changes. The S_3–S_B transition temperatures measured by D.T.A. again alternate regularly, and in the same manner as for the S_B–S_A temperatures. This series is a further illustration(3) that smooth curve relationships between temperatures for like transitions and alkyl chain length apply to S–S as well as to other types of mesophase transitions.

In addition to the transition temperatures determined by D.T.A., Table 1 gives the enthalpies and entropies for the various transitions for the homologues.

Figure 3 presents a D.T.A. trace for one of the esters and shows the general increase in enthalpy that occurs on passing from S_3–S_B to S_B–S_A to S_A–I transitions. Though plots of the enthalpies or associated entropies for the various types of transition against alkyl chain length indicate general trends along the series, the values do not alternate regularly like the transition temperatures; this may be because of inherent inaccuracies in the measurements.

The S_3 phase for these esters is clearly neither of the *A* type nor of the *B* type in which the molecules are normal to the layer planes, and it is immiscible with the S_C phase of *p*-*n*-octyloxybenzoic acid.(4) Moreover, the phase is not optically isotropic and is not of the S_D type.

Paramorphosis of the smectic textures is common for all the esters. On cooling the amorphous liquid, S_A adopts a fan texture which is retained with a decrease in the number of lines in the S_B phase. This same texture persists in S_3, but concentric arcs now cross the fans and characterize the phase (Fig. 4a). When these arcs are less well defined, the change accompanying this transition is difficult to detect microscopically. The crystals then form on further cooling, and they too adopt a fan texture; therefore the same mesophase textures and the same problems of paramorphosis are encountered on heating cycles.

Methods to produce different textures for the S_B and S_3 phases have, however, been successful. In some cases, S_B has been induced to adopt a poorly defined mosaic texture, and when S_3 replaces this, the texture is unchanged except for narrowly spaced lines which now cross the mosaic areas. The S_A phases of several of the esters were obtained almost completely homeotropic by making a cover slip

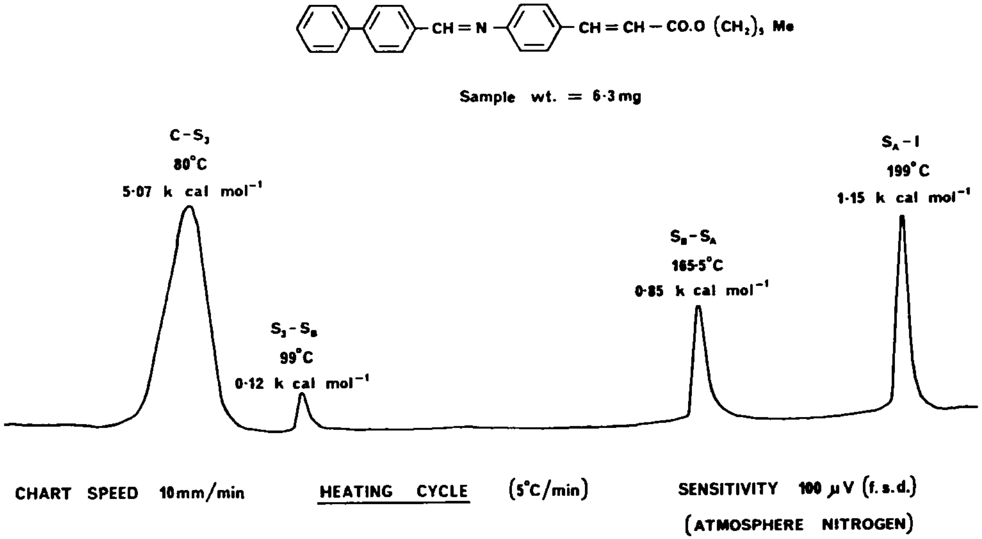


Figure 3. Differential thermal analysis trace (heating cycle) for *n*-hexyl 4-(*p*-phenylbenzylideneamino)cinnamate.

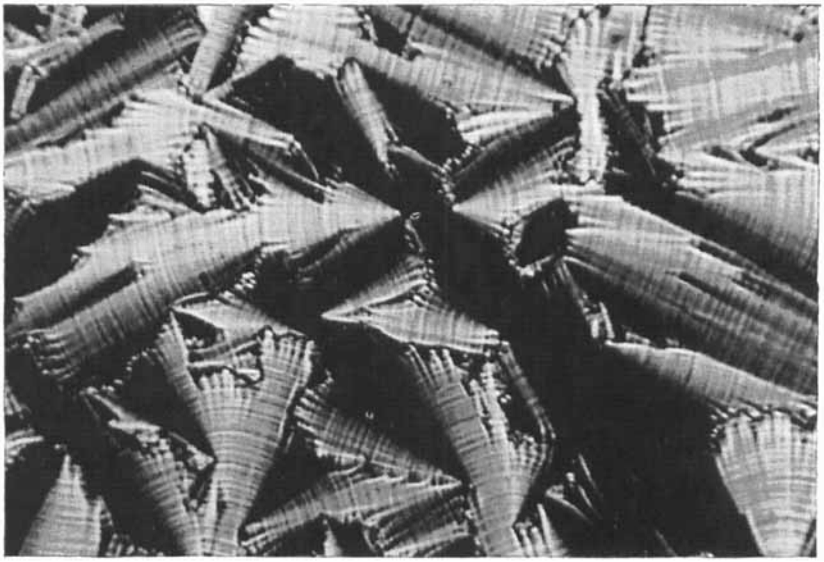


Figure 4a. Fan texture of the S_3 phase of a n-alkyl 4-(p-phenylbenzylideneamino)cinnamate showing the concentric arcs (× 32); crossed polars.

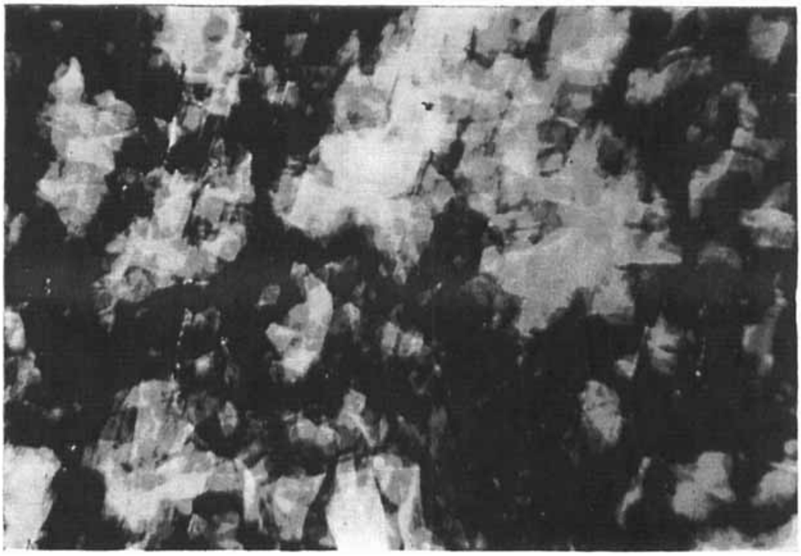


Figure 4b. Birefringent texture of the S_3 phase of a n-alkyl 4-(p-phenylbenzylideneamino)cinnamate obtained on cooling from the homeotropic S_B phase (× 37); crossed polars.

displacement to the preparations. This homeotropy was maintained in the S_B phase. On further cooling, S_3 appeared as a birefringent phase (Fig. 4b); heating regenerated the homeotropic S_B phase. The plate-like texture of smectic 3 in Fig. 4b does not seem to resemble closely the texture of any other smectic modification that has been reported. The black areas are not optically isotropic; this is readily shown using a quartz sensitive tint plate. On rotation of the sample between crossed polars, the black and white areas become white and black, respectively, at 45° intervals.

The homeotropic S_A and S_B phases gave positive uniaxial interference figures, whereas the birefringent texture of S_3 shown in Fig. 4b gave a positive biaxial interference figure. The biaxial properties indicate that the long molecular axes in S_3 are tilted with respect to the layer planes, and preliminary X-ray studies by Dr. J. Lydon at Leeds lend strong support to this conclusion. Since the S_3 phase forms on cooling from a uniaxial S_B phase in which the molecules are presumably ordered in the planes of the smectic layers, the S_3 phase would seem to be very similar to the hexagonally ordered, tilted S_B phase found by Levelut and Lambert(5) for terephthalylidene-bis-4-*n*-butylaniline (TBBA).

However, as reported by W. Z. Urbach and J. Billard in a paper presented at the Fourth International Liquid Crystal Conference held at Kent State University, Ohio, U.S.A. in 1972, the tilted S_B phase of TBBA is separately miscible with an S_B phase in which the molecules are normal to the layer planes and with the new S_H phase found by de Vries and Fishel(14) for ethyl 4-(*p*-*n*-butylbenzylidene)-aniline. Since S_3 is immiscible with an S_B phase in which the molecules are normal to the smectic layers (it is separated from such a phase by a first order S_3–S_B transition), it appears that S_3 must be different from such a phase and also from the tilted S_B phase of TBBA and the S_H phase. S_3 must therefore be of the S_E, S_F or S_G type or be a new type of smectic phase. A very recent personal communication from Professor H. Sackmann of the Martin-Luther-Universität at Halle has indicated, however, that the S_3 phases of our *n*-heptyl and *n*-decyl 4-(*p*-phenylbenzylideneamino)cinnamates are separately miscible with the S_E phase of one of his compounds.(15) If we accept this evidence, despite the doubt cast on the concept of co-miscibility by the work of Urbach and Billard which has shown that mesophases with different physical characteristics can be miscible, then the S_3 phases belong to the S_E class which must therefore be characterized by biaxial properties and a tilted arrangement of the molecules in the layers. Confirmation of this assignment to the S_E class and evidence showing how the S_3 (S_E) phases differ structurally from tilted S_B phases and from the S_H phase must however await the results of the more detailed X-ray studies of these phases now being made by Dr. J. Lydon at the University of Leeds.

The occurrence of this S_3 phase is not confined to the series under discussion; it has been detected frequently⁽³⁾ in less extended series of ω-phenylalkyl and branched chain alkyl 4-(*p*-phenylbenzylideneamino)cinnamates, and as reported elsewhere,⁽⁶⁾ in several heterocyclic mesogens. If the phases are indeed of the S_E type, then the number of known examples of compounds giving this type of phase has suddenly been increased from 4 to about 40.

2. DI-(-)2-METHYLBUTYL TEREPHTHALYLIDENE-BIS-*p*-AMINOBENZOATE

The racemic modification is nematic (C–N, 123 °C; ΔH, 6.97 kcal mol^{-1}; N–I, 184 °C; ΔH, 0.05 kcal mol^{-1}) and the (-) diastereoisomer is cholesteric (C–Ch, 123 °C; ΔH, 8.43 kcal mol^{-1}; Ch–I, 184 °C; ΔH, 0.07 kcal mol^{-1}). Optical microscopy reveals no unusual properties for the nematic phase of the racemic modification. When crystals of the optically active isomer are heated, they give a mesophase which, after displacement of the cover slip, has a typical cholesteric plane texture (yellow to the eye in reflected light). Between crossed polars, the uniform areas are green (becoming blue at higher temperatures) and are separated by typical alignment discontinuities. Two reversible transitions occur before the amorphous liquid is formed; these arise within 0.5–1 °C of the final change which gives the amorphous liquid. The first transition gives a fairly uniform blue " phase " in which green streaks are observed; these correspond to the alignment discontinuities in the preceding plane texture. This blue + green " phase " is however predominantly green when it is obtained by heating the " focal-conic " texture—see Fig. 5. Further heating gives the second transition to a uniformly pale blue " phase " which is optically isotropic and less readily observed; this then merges into

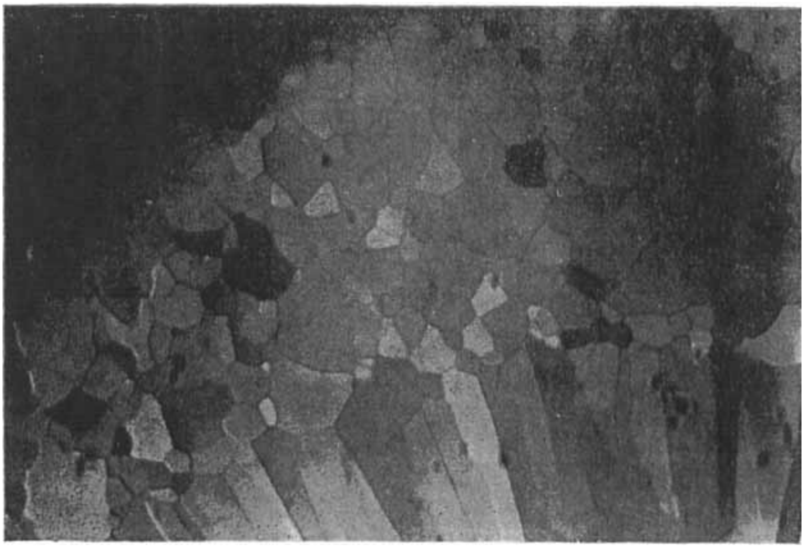


Figure 5. The transition from the " focal-conic " texture of the cholesteric mesophase (lower left hand corner) of di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate to the blue + green " phase " (× 37); crossed polars.

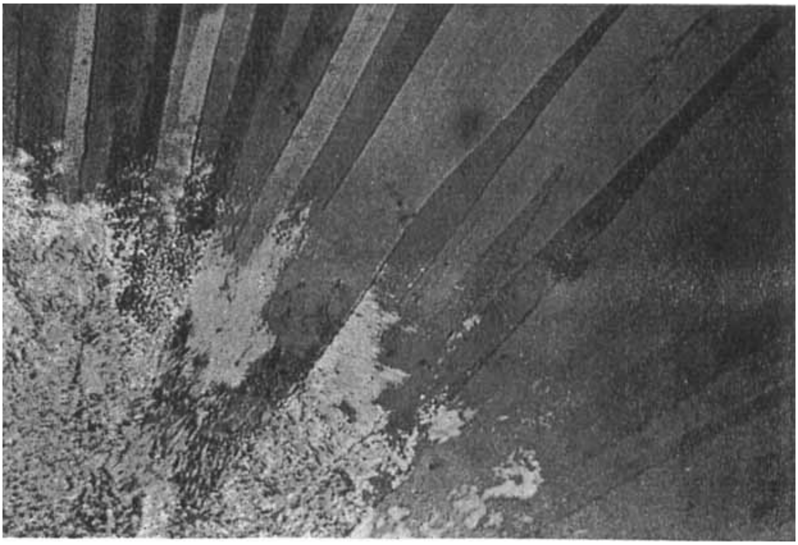


Figure 6. Transitions from the blue + green " phase " of di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate—lower semi-circle—to the blue isotropic " phase "—seen in the black and white photograph only as a milky band surrounding the semi-circle—to the amorphous isotropic liquid—top left and right hand corners (× 37); crossed polars.

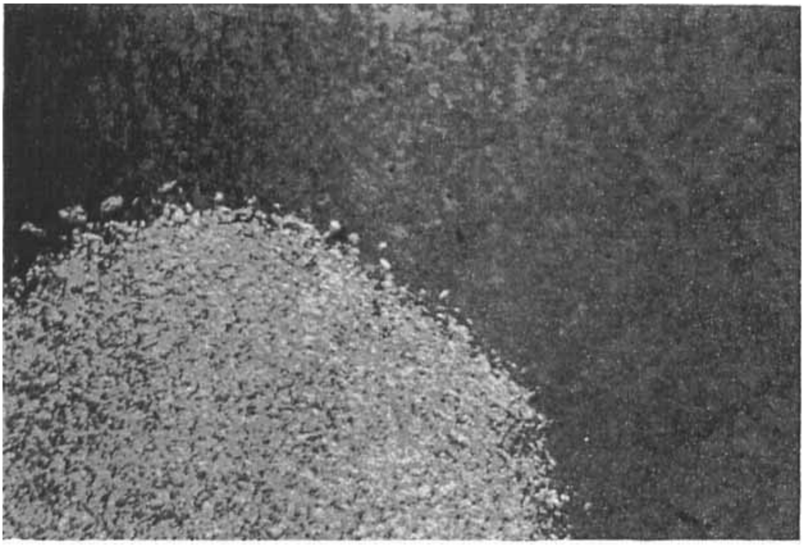


Figure 7. Polygonal shaped areas and striped regions of the blue + green " phase " of di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate obtained from the blue isotropic " phase " top left hand corner (× 37); crossed polars.

Figure 8. Stripes or blades of the blue + green " phase " of di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminobenzoate showing saw-like edges. The " focal-conic " texture of the cholesteric phase is forming in the lower left hand corner (× 37); crossed polars.

the amorphous liquid at a slightly higher temperature. Figure 6 shows the transition from the green + blue " phase " to the blue isotropic " phase " and thence to the amorphous liquid. On cooling, the blue isotropic " phase " appears first (without supercooling) and gives the blue + green " phase " (again without supercooling). The latter " phase ", when obtained by cooling, has a less uniform appearance; the texture in fact varies appreciably, but always contains blue and green areas. Sometimes the blue and green areas have quite regular polygonal shapes as shown in the middle region of Fig. 7 in which the upper left hand corner is the blue isotropic " phase "; sometimes the " phase " forms as blue and green stipes or blades (see the bottom part of Fig. 7) and occasionally these have saw-like edges (Fig. 8). Rotation of the stage does not cause extinction or change the colours. On further cooling, the blue + green " phase " gives the " focal-conic " cholesteric texture. In Fig. 8, the " focal-conic " texture is developing in the lower left hand corner; a cover slip displacement changes this to the plane texture, which, as stated above, gives the same sequence of changes on heating.

Thus,

$$\begin{tikzcd}
\text{Cholesteric plane texture} \arrow[r, "T_1"] & \text{Blue + green `` phase ''} \arrow[r, shift left, "T_2"] \arrow[d, shift right, "<T_1"'] & \text{Blue isotropic `` phase ''} \arrow[l, shift left, "T_2"] \arrow[r, shift left, "T_3"] & \text{Amorphous liquid} \arrow[l, shift left, "T_3"] \\
& \text{`` Focal-conic '' cholesteric texture} \arrow[ul, "\text{cover slip displacement}"] \arrow[u, shift right, "T_1"'] & &
\end{tikzcd}$$

These changes are visible to the eye, in reflected light, when a thin film of the amorphous liquid is cooled. The blue isotropic " phase " is discernible as a narrow fringe preceding the blue + green " phase " (a narrow lime green band) which is followed by the opaque, yellow " focal-conic " texture.

It is apparent therefore that the molecular organization of the plane or " focal-conic " texture breaks down in steps to give the amorphous liquid, and that cooling gives reversal of these steps. Separate resolved peaks are not observed by D.T.A. for these closely occurring transitions, but the small Ch–I peak does have a noticeable wing on the low temperature side.

Although little is yet understood about these transitions, and some doubt must attach to whether distinct phases are involved, it seemed of interest to report the observations and consider whether other cholesterogens behave similarly. In this connection, it is noted that (-)2-methylbutyl terephthalylidene-bis-*p*-aminocinnamate behaves in a similar manner, but the transition temperatures are much higher and decomposition interferes with the observations. However, this ester confirms that the phenomena observed are not of an isolated nature.

Consider next compounds such as the cholesteryl *n*-alkanoates or cholesteryl *p*-*n*-nonylphenyl carbonate. On cooling, the amorphous liquid of such an ester first gives a blue isotropic liquid which then gives the " focal-conic " cholesteric texture.(7,8,9) This blue isotropic liquid is apparently somewhat different from that of the diester discussed above, for the former is not visible between crossed polars. Although some debate has centred around the question as to whether the blue isotropic " phase " of a cholesteryl ester is formed during heating cycles from either the plane or " focal-conic " textures, recent careful experimental studies by Price and Wendorff(10) apparently show that it is, and they and others have observed white regions or platelets which develop at a slightly lower temperature within the blue " phase " of cholesteryl myristate. Price and Wendorff(10) have also obtained evidence that the transition giving this white " phase " is reversible at 83 °C. These authors showed that the change from the white " phase " to the blue " phase " is not accompanied by detectable changes in volume or expansion coefficient, and they classify the change as one of texture and not of structure. Saupe(8) has proposed that the blue isotropic liquid of cholesteryl *p*-*n*-nonylphenyl carbonate may involve a cubic arrangement of micelles consisting of parallel molecules and having an internally twisted structure in order to account for the optical activity of the liquid which is higher than that of the amorphous liquid.

In the case of the optically active diester discussed earlier, the long range order of the " focal-conic " cholesteric phase also apparently builds up from the amorphous liquid in two steps. The higher temperature blue " phase " may be related to the blue, isotropic, cubic " phase " of the cholesteryl esters and the lower temperature blue + green " phase " may have a different symmetry—possibly hexagonal—and may be related to the white, platelet " phase " of cholesteryl myristate. It is noted that when a quartz sensitive tint plate is used, the blue regions of the blue + green " phase " assume a slightly less deep red colour than that given by the blue isotropic " phase " itself.

3. (-)2-METHYLBUTYL 4-(*p*-SUBSTITUTED BENZYLIDENEAMINO)-CINNAMATES

Four optically active esters with *p*-substituents were next studied with particular reference to the cholesteric to amorphous liquid transition. All these pale yellow compounds exhibited cholesteric mesophases and Table 2 gives the results obtained by D.T.A. and microscopy.

TABLE 2 Temperatures (T) and enthalpies (ΔH) of transition for (-)2-methylbutyl 4-(*p*-substituted-benzylideneamino)cinnamates[e]

	C–S_2, S_1 or Ch		S_2–S_1[d]		S_1–Ch		Ch–I	
Substituent	T[a]	ΔH[a]	T	ΔH	T	ΔH	T	ΔH
CN	94.0	5.02	—	—	—	—	110	0.07
NO_2	83.5	6.58	—	—	—	—	85	0.03
Cl[b]	64.5	2.25	—	—	—	—	69	0.11
MeO[c]	44.0	4.77	60	0.10	80	0.40	100	0.39

[a] T(°C); ΔH (kcal mol^{-1}). Temperatures measured by optical microscopy.

[b] As reported elsewhere,(11) this ester exists in two separate crystal forms with different melting points; the mesophase is monotropic with respect to the higher melting crystal form (C–I, 81 °C; ΔH, 5.44 kcal mol^{-1}). Apparently the higher melting crystal form is dimorphic with a crystal–crystal transition at 52 °C; in the earlier work,(11) this crystal–crystal change was thought to involve a change from the lower to the higher melting crystal form.

[c] D.T.A. now reveals that this ester has a polymorphic smectic modification additional to the phases reported elsewhere.(11)

[d] Based only on the optical textures, S_1 is S_A and S_2 is S_B.

[e] All four compounds have been previously reported;(11) the constants quoted were:

CN	C–Ch, 93.5 °C; Ch–I, 108 °C
NO_2	C–Ch, 82.5 °C; Ch–I, 84 °C
Cl	C–I, 80 °C or C–Ch, 66.5 °C; Ch–I, 69.5 °C
MeO	C–S, 54 °C; S–Ch, 76.5 °C; Ch–I, 98 °C.

In all cases, the enthalpies for the Ch–I transitions were very small and difficult to measure reproducibly; the peaks again had noticeable wings on their low temperature sides. Although no sub-peaks were observed, careful optical microscopy showed that each cholesteric phase (either as the plane or the " focal-conic " texture) changed to the amorphous liquid in a complex manner involving distinct and reversible changes of either phase or texture—at present it is not possible to be certain which.

The cyano-, chloro- and methoxy esters behave similarly when either the plane or the " focal-conic " textures are heated. In the case of the cyano-ester, the first " phase " is yellow-ochre in colour and shows the alignment discontinuities of the preceding plane texture when viewed between crossed polars. The corresponding " phase " for the chloro-ester is green-blue; this " phase " is seen forming from the " focal-conic " texture in Fig. 9. A sharp boundary (Fig. 9) separates this " phase " from the next " phase " which has a mosaic pattern. This mosaic varies in both the magnitude of the individual areas of the mosaic and their colour according to heating rate and the compound involved; slower heating gives a coarser mosaic pattern. These changes are reversible on cooling, giving ultimately the " focal-conic " texture; only the change to the " focal-conic " texture involves supercooling.

When the mosaic of the higher temperature " phase " is coarse, i.e., when it is formed either at very slow heating or cooling rates, it is clear that the lower temperature " phase " is also a mosaic, but one which has a veiled or clouded appearance. When this " phase " is heated, the transition involves a receding of the veil giving the clear mosaic of the higher temperature " phase ". This is demonstrated particularly clearly in the case of the methoxy-ester.

Very slow heating of the "focal-conic" texture (right hand side of Fig. 10) produces a well-defined, but veiled mosaic (left hand side of Fig. 10); the veil then moves away giving the well developed, clear mosaic shown in Fig. 11 (the amorphous liquid is on the extreme left hand side). Heating the plane texture of the methoxy-ester gives the same effects, except that a band of spherulites occurs on the boundary of the plane texture and the lower-temperature, veiled mosaic. These spherulites have also been detected on heating the plane textures of the chloro- and cyano-esters. The spherulites are

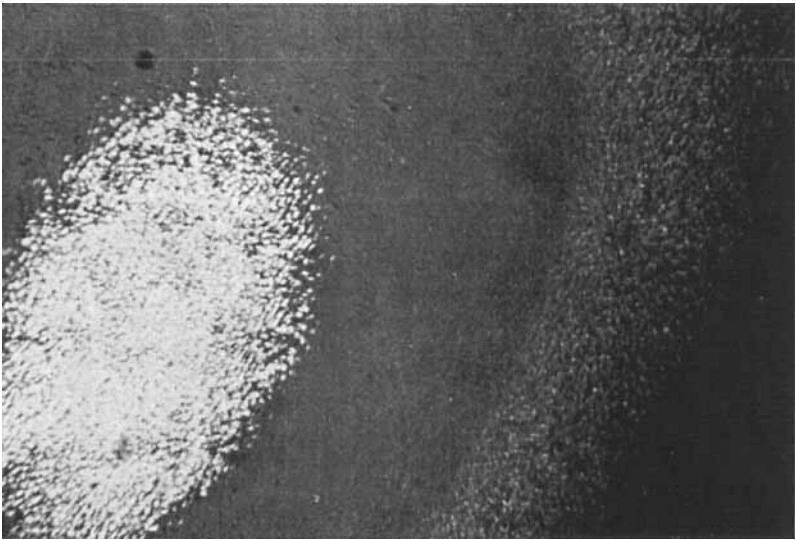


Figure 9. Transitions observed on heating the " focal-conic " phase (extreme left) of (-)2-methylbutyl 4-(*p*-chlorobenzylideneamino)cinnamate. The sequence of phases from extreme left to right is " focal-conic " phase, veiled mosaic " phase ", clear mosaic " phase " and amorphous, isotropic liquid (× 37); crossed polars.

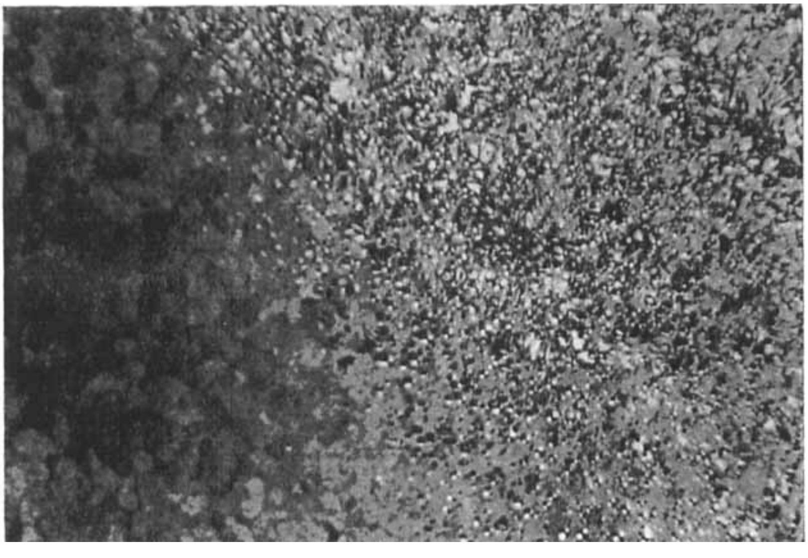


Figure 10. The transition from the " focal-conic " cholesteric phase (right hand side) to the veiled mosaic " phase " (left hand side) on heating (-)2-methylbutyl 4-(*p*-methoxybenzylideneamino)cinnamate (× 37); crossed polars.

Figure 11. Clear mosaic " phase " of (-)2-methylbutyl 4-(*p*-methoxybenzylideneamino)cinnamate passing to the amorphous, isotropic liquid on the left hand side (× 37); crossed polars.

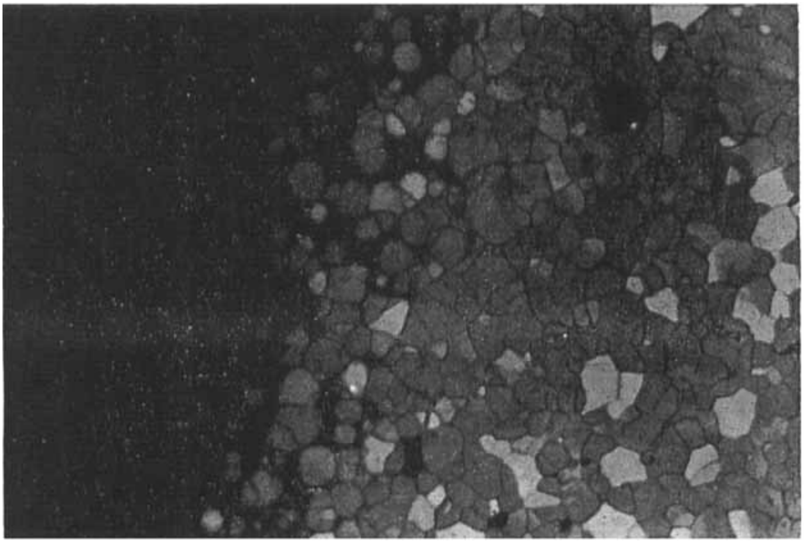


Figure 12. Clear mosaic " phase " of (-)2-methylbutyl 4-(*p*-nitrobenzylideneamino)cinnamate growing in the green isotropic " phase " on the left hand side. The latter " phase " cannot be distinguished by black and white photography from the amorphous, isotropic liquid; the colour between crossed polars is dark olive green (× 37).

more difficult to detect at the boundary of the " focal-conic " texture and the veiled mosaic " phase " but there is some evidence that they occur there also.

These changes observed either on heating the " focal-conic " or plane textures or on cooling the amorphous liquids of these esters occur within a 0.5 to 1 °C range of the final mesophase–amorphous liquid transition. It should be emphasized that the colours of the " phases " vary quite appreciably from compound to compound. For the cyano-ester, the veiled mosaic is of a yellow-ochre colour and the clear mosaic is blue and red, irrespective of whether these arise from " focal-conic " or the plane texture. The chloro-ester gives a blue veiled mosaic with a pink fringe before giving a clear yellow mosaic, when the plane texture is heated. On heating the " focal-conic " texture of this chloro-ester, the veiled mosaic is a green-blue in colour and the mosaic consists of blue and yellow regions. Similarly coloured " phases " are obtained on heating either the " focal-conic " or the plane texture of the methoxy-ester; the veiled mosaic is green with brown patches and the clear mosaic is green and orange/brown.

The nitro-ester behaves differently, but only on cooling. A green, homogeneous, isotropic " phase " first separates from the amorphous liquid. A well defined mosaic next develops in this " phase " (Fig. 12), and then, at a slightly lower temperature, this mosaic clouds over to give the veiled mosaic. If the cooling rate is too fast, the development of the mosaics in the green isotropic " phase " is not seen. This, together with the fact that the green isotropic " phase " is not formed on heating, suggests that the green " phase " is monotropic with respect to the higher temperature mosaic " phase " whose formation must involve some degree of supercooling.

These cholesteric cinnamate esters illustrate again that the overall change from the plane or " focal-conic " texture to the amorphous liquid is a complex process involving two intermediate states which could be distinct phases. In the case of the nitro-ester, three such intermediate states are involved on the cooling cycle.

Whatever the nature of the changes that occur during the breakdown of the " focal-conic " or the plane texture to give the amorphous liquid and during the build up of the long range order from the amorphous liquid, it is clear that they are highly sensitive to the chemical constitutions of the compounds involved. Thus the diester, the cholesteryl esters and the cinnamate esters all behave differently, and as mentioned above, the nitro-ester is different from the other three cinnamate esters.

It is interesting to note that Stumpf(12) originally stated that the cyano-ester of the cinnamate series gave a second cholesteric phase, but this was disputed by Friedel(13) who concluded (probably wrongly) that Stumpf was confusing the plane and "focal-conic" textures of the cholesteric mesophase. It seems probable that Stumpf observed one of the intermediate "phases" under discussion now, and that the significance of his finding was lost because of Friedel's comments.

In conclusion, it seems that more detailed investigations of the overall change from cholesteric plane or "focal-conic" texture to amorphous liquid may prove of value in leading to a better understanding of the manner in which the unique molecular organization of the cholesteric phase breaks down on heating and reforms on cooling from the disordered amorphous liquid.

3. Experimental

1. MATERIALS

All of the *n*-alkyl *p*-aminocinnamates were prepared from the commercially available *p*-aminocinnamic acid hydrochloride by direct esterification using the Fischer-Speier method, with the exception of the *n*-nonyl ester. This ester and the (-)2-methylbutyl esters of *p*-aminobenzoic acid and *p*-aminocinnamic acid were prepared by an alternative route that was more economical in the amounts of the alcohols used. *p*-Nitrobenzoyl chloride or *p*-nitrocinnamoyl chloride, prepared from the corresponding nitro-acid and thionyl chloride, was interacted with the alcohol (nonan-1-ol or (-)2-methylbutan-1-ol) using pyridine as solvent. *n*-Nonyl *p*-nitrocinnamate (m.p. 47–47.5 °C) was purified by crystallization from a mixture of benzene and light petroleum (b.p. 40–60 °C). (-)2-Methylbutyl *p*-nitrobenzoate and *p*-nitrocinnamate were obtained as oils from the reaction mixtures. The esters were purified by fractional distillation under vacuum. (-)2-Methylbutyl *p*-nitrobenzoate and the racemate remained as oils at room temperature; the corresponding active cinnamate ester solidified and had m.p. 42–43 °C. The nitro-esters were reduced by heating with iron pin dust in a mixture of 20% aqueous acetic acid and ethanol, following the procedure of Semonsky and Kunak.(16)

The amino-esters prepared by either of the above methods were purified by crystallization from light petroleum (b.p. 40–60 °C), from benzene or from a mixture of these two solvents. In the case of (-)2-methylbutyl *p*-aminobenzoate and the racemate, the esters were first purified by fractional distillation under vacuum. The distillates solidified and were crystallized from a mixture of benzene and light petroleum (b.p. 40–60 °C).

In the case of known amino- and nitro-esters, agreement with literature m.p.s. was obtained. Melting points for the intermediate amino-esters are given in Table 3; elemental analyses for new amino-esters are in Table 4.

TABLE 3 Melting points for esters of *p*-aminocinnamic acid[a]

Alkyl group	m.p. (°C)	Alkyl group	m.p. (°C)
Methyl	127–128	*n*-Heptyl	78.0–78.5
Ethyl	70– 70.5	*n*-Octyl	84.5–85.0
n-Propyl	92– 93	*n*-Nonyl	80.0–80.5
n-Butyl	85– 86	*n*-Decyl	87.0–88.0
n-Pentyl	65– 66	(-)2-Methylbutyl[b]	83.0–84.0
n-Hexyl	79– 80		

[a] Three of these esters have been reported previously:

1. Methyl: m.p. 128–129 °C (Einhorn, M. and Oppenheimer, E., *Ann.* **311**, 158 (1900).
2. Ethyl: m.p. 68–69 °C
3. Butyl: m.p. 85–86 °C

} Semonsky, M. and Kunak, J., *Chem. Listy* **47**, 598 (1953).

[b] The corresponding benzoate ester, (-)2-methylbutyl *p*-aminobenzoate, had m.p. 46–47 °C; the racemate had m.p. 37–38 °C.

The pure amino-esters (1 mol) were then interacted separately with the required aldehyde—*p*-cyanobenzaldehyde, *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, *p*-methoxybenzaldehyde or biphenyl-4-carboxaldehyde (1.1 mol in each case) or terephthalaldehyde (0.55 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 isolated and crystallized until their m.p.s. and liquid crystal transition temperatures were constant; the solvents used were ethanol or a mixture of benzene and light petroleum (b.p. 40–60 °C).

The melting points for the various Schiff's bases, their liquid crystal transition temperatures and the enthalpies of the various transitions are recorded in the text of the Results and Discussion section or in Tables 1 or 2.

Di-(-)2-methylbutyl terephthalylidene-bis-*p*-aminocinnamate was also prepared and purified, but it decomposed at the cholesteric–amorphous liquid transition. The constants determined by D.T.A. were C–S, 134 °; S–Ch, 234 °; Ch–I, 283 °C (decomp.).

Elemental analyses for new Schiff's bases are in Table 5.

2. METHODS

Differential thermal analysis was carried out using a low temperature differential thermal analyser (LDT 671) and two-channel flat bed recorder (Stanton Redcroft Ltd., Copper Mill Lane, London). A 5 °C/min programme was used for heating and cooling cycles. The transition temperatures and the enthalpies of transition were obtained from the D.T.A. traces. Transition temperatures were reproducible to ± 0.25 °C; for enthalpies of transition, the reproducibility was about ± 10%.

The transition temperatures (reproducible to ± 0.25 °C) were also checked and the mesophase textures examined using a polarizing

TABLE 4 Elemental analyses for new Alkyl *p*-aminocinnamates (I) and for (-)2-Methylbutyl *p*-aminobenzoate (II) and the racemate

Compound	Found (%) C	H	N	Formula	Required (%) C	H	N
I (Propyl)	70.3	7.5	6.9	$C_{12}H_{15}NO_2$	70.3	7.3	6.8
I (Pentyl)	72.4	8.2	6.2	$C_{14}H_{19}NO_2$	72.1	8.2	6.0
I (Hexyl)	72.9	8.6	5.5	$C_{15}H_{21}NO_2$	72.8	8.5	5.7
I (Heptyl)	73.4	8.7	5.4	$C_{16}H_{23}NO_2$	73.6	8.8	5.4
I (Octyl)	74.0	9.1	5.2	$C_{17}H_{25}NO_2$	74.2	9.1	5.1
I (Nonyl)	75.0	9.5	4.8	$C_{18}H_{27}NO_2$	74.7	9.3	4.8
I (Decyl)	75.4	9.7	4.6	$C_{19}H_{29}NO_2$	75.3	9.6	4.6
I ((-)2-Methylbutyl)	72.2	8.0	6.0	$C_{14}H_{19}NO_2$	72.1	8.2	6.0
II	69.4	8.1	6.7	$C_{12}H_{17}NO_2$	69.6	8.2	6.7
II (racemate)	69.5	8.3	6.5	$C_{12}H_{17}NO_2$	69.6	8.2	6.7

TABLE 5 Elemental analyses for new *n*-Alkyl 4-(*p*-phenylbenzylideneamino)-cinnamates and for Di-2-methylbutyl terephthalylidene-bis-*p*-amino-benzoate (III, active and racemic ester) and -cinnamate (IV, active ester)

Compound	Found (%) C	H	N	Formula	Required (%) C	H	N
Propyl	81.0	6.2	3.5	$C_{25}H_{23}NO_2$	81.3	6.2	3.8
Pentyl	81.4	6.8	3.3	$C_{27}H_{27}NO_2$	81.6	6.8	3.5
Hexyl	81.6	7.0	3.4	$C_{28}H_{29}NO_2$	81.8	7.0	3.4
Heptyl	81.9	7.4	3.2	$C_{29}H_{31}NO_2$	81.9	7.3	3.3
Octyl	82.2	7.8	3.0	$C_{30}H_{33}NO_2$	82.0	7.5	3.2
Nonyl	81.9	7.7	2.8	$C_{31}H_{35}NO_2$	82.1	7.7	3.1
Decyl	82.4	8.0	3.0	$C_{32}H_{37}NO_2$	82.2	7.9	3.0
III (active)	75.1	7.2	5.3	$C_{32}H_{36}N_2O_4$	75.0	7.0	5.5
III (racemic)	74.9	7.1	5.3	$C_{32}H_{36}N_2O_4$	75.0	7.0	5.5
IV (active)	76.4	7.0	4.9	$C_{36}H_{40}N_2O_4$	76.6	7.1	4.9

microscope in conjunction with a heated stage (C. Reichert, Optische Werke A.G., Wien, Austria). Photomicrographs were obtained using a Leica camera.

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