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The Liquid Crystalline Properties of Alkyl, Aryl and Arylalkyl 4-*p*-Substituted-benzylideneamino-cinnamates and α-methylcinnamates†

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Abstract—Five homologous series (methyl to *n*-decyl) of *n*-alkyl 4-*p*-substituted-benzylideneaminocinnamates with *p*-substituents = CN, NO_2, MeO, MeCO.O and Ph have been prepared and the liquid crystalline properties established. The relative thermal stabilities of the mesophases of the esters with different *p*-substituents are in keeping with established orders of terminal group efficiency, but in certain of the series the trends in transition temperatures with increasing alkyl chain length give rise to novel smooth curve relationships.

The effects of branching the alkyl chain have been investigated using alkyl groups containing three, four, five and six carbon atoms. The effects of a methyl substituent on the first carbon of the alkyl chain are particularly marked, nematic properties suffering most dramatically. The behaviour is discussed in terms of intramolecular steric effects.

The effects of having a group other than methyl as the end unit of a *n*-alkyl chain have been examined by studying the liquid crystalline tendencies of ω-phenylalkyl and ω-isopropylalkyl 4-*p*-substituted-benzylideneaminocinnamates. The profound alternation in nematic properties, leading in some series to an alternation between smectic/nematic and purely smectic behaviour, is discussed in terms of molecular structural factors.

Some esters of 4-*p*-substituted-benzylideneamino-α-methylcinnamic acids are included in the survey.

1. Introduction

This paper describes studies of the liquid crystalline properties of Schiff's bases prepared by condensing *p*-substituted benzaldehydes with a range of esters of *p*-aminocinnamic acid. The compounds are

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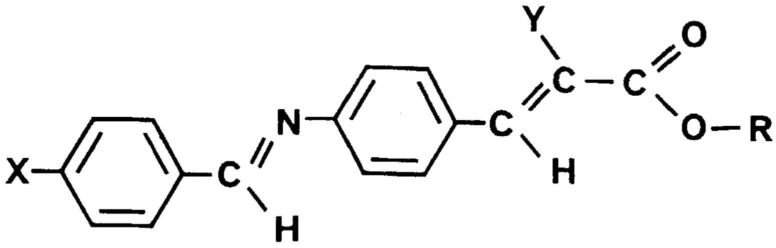
† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

represented by structure (I). The substituent X was chosen from the group CN, NO_2, MeO, MeCO.O, Ph and the ester group R was n-alkyl or branched alkyl, phenyl or ω-phenylalkyl, or in a limited number of cases cyclohexyl or ω-cyclohexylalkyl. In the majority of cases, Y was H, but a few α-methylcinnamates ($Y = \text{Me}$) were included with the compounds surveyed.



I

The liquid crystalline properties of some of these Schiff's bases, particularly those exhibiting optical activity because of the presence of a centre of asymmetry in the ester group R, were reported at the Second International Liquid Crystal Conference in 1968.(1,2) More recently, Leclerq, Billard and Jacques(3) have published transition temperatures and heats of transition for a further fifteen of these Schiff's bases. Although such Schiff's bases give liquid crystals at moderate temperatures, none of the compounds examined in these earlier studies or in the work now reported has given a liquid crystal stable at room temperature. Indeed, Leclerq *et al.*(3) remark that compounds of this type are not suitable for the production of liquid crystals at low temperatures, and that because of this and the relative instability of the Schiff's bases, they intended to direct their attention to other liquid crystalline systems. The main object of our studies was, however, to examine in a systematic manner the effects of terminal substituents on liquid crystalline behaviour, and from this point of view system (I) is ideally flexible, readily permitting a study of the effects of a range of terminal groups X and R on the mesomorphic properties. Although some of the compounds we have examined were somewhat unstable, this has not been found to be a general problem, and more will be said about this point in due course.

As observed too by Leclerq *et al.*,(3) many of these Schiff's bases give complex polymorphic changes, and an example of this will be quoted. Because of the large number of compounds under study, detailed optical studies using hot stage microscopy are as yet incomplete. These are certainly necessary to elucidate the polymorphic changes which do occur, and projected studies by differential scanning calorimetry will also be important in this respect. It should be emphasized therefore that the physical constants quoted in this paper are those obtained by the normal capillary melting point method. However, for those compounds which have been examined by hot stage microscopy, no discrepancies between the transition temperatures measured and those obtained by the capillary method have been found.

On examining the literature for known compounds of structure (I), it became apparent that even for the n-alkyl esters, many gaps in the homologous series for the different substituents X existed. Moreover, the trends in the physical constants reported for some of the more complete series, and in some cases the identities of the mesophases themselves seemed doubtful. Since we planned to make the n-alkyl esters our basis for comparison in investigating the effects on mesomorphic behaviour of chain branching and other modifications to the n-alkyl group, it was necessary to prepare and examine at least the first ten homologues (methyl to n-decyl) for each of the five terminal groups X in which our interest lay, i.e., X = CN and NO_2, to give nematic systems, X = Ph, to give smectic and nematic liquid crystals of high thermal stability, and X = MeO and MeCO.O, to provide lower melting liquid crystalline systems.

LIQUID CRYSTALLINE PROPERTIES OF n-ALKYL ESTERS OF SYSTEM (I)

The melting points and liquid crystal transition temperatures—measured in all cases by the capillary melting point method—for each of the five (X = CN, NO_2, Ph, MeO, MeCO.O) homologous series (methyl to n-decyl) of n-alkyl esters of system (I)—Y = H, are given in Tables 1 to 5, in which the following abbreviations have been used:(4)

C, crystal; S, smectic, N, nematic liquid crystal; I, amorphous isotropic liquid.

Where more than one smectic state occurs in a series, the higher temperature smectic state has been called S_1 and the lower temperature state S_2. Since hot stage microscopic studies of the liquid crystals are still incomplete, classification of the polymesomorphic smectic states in terms of the various accepted⁽⁵⁾ smectic forms (A, B, C, etc.) has not yet been determined.

As expected from earlier studies,⁽¹⁾ terminal CN and NO_2 groups

Table 1
System (I); $X = CN$; $Y = H$

	Temperature (°C) of transition		
R = Alkyl	C–S or N	S–N	N–I
Methyl	180.5	—	231.5
Ethyl	152	—	178.5
n-Propyl	102	—	158
n-Butyl	108.5	—	132.5
n-Pentyl	74	—	133
n-Hexyl	76.5	—	122.5
n-Heptyl	78	—	121.5
n-Octyl	64	—	114.5
n-Nonyl	65	81.5	113.5
n-Decyl	67	95	110.5

Table 2
System (I); $X = NO_2$; $Y = H$

	Temperature (°C) of transition		
R = Alkyl	C–I	C–N	N–I
Methyl	—	211.5	214 (dec.)
Ethyl	177.5	—	—
n-Propyl	—	112.5	135
n-Butyl	—	86	112.5
n-Pentyl	—	90.5	112
n-Hexyl	—	67.5	100
n-Heptyl	—	88.5	102.5
n-Octyl	—	83	96.5
n-Nonyl	—	79	97.5
n-Decyl	—	75	96

strongly promote nematic properties; no smectic properties arise with $X = NO_2$, and only with the longest *n*-alkyl chains (R = *n*-nonyl and *n*-decyl) are smectic states given when X = CN. The N–I temperatures for the cyano-compounds are appreciably higher than for the nitro-compounds, and therefore X = CN stabilizes both smectic and nematic states relative to $X = NO_2$. For both series, plots of transition temperature *v* alkyl chain length are similar. The N–I temperatures lie on two smooth curves which fall steeply at first and then level out as the series is ascended. The upper curve is for the esters with an odd number and the lower curve for the esters with an even number of carbons in the alkyl chain. This typical behaviour, showing the decreasing degree of alternation of the N–I temperatures as the chain lengthens, is illustrated in Fig. 1

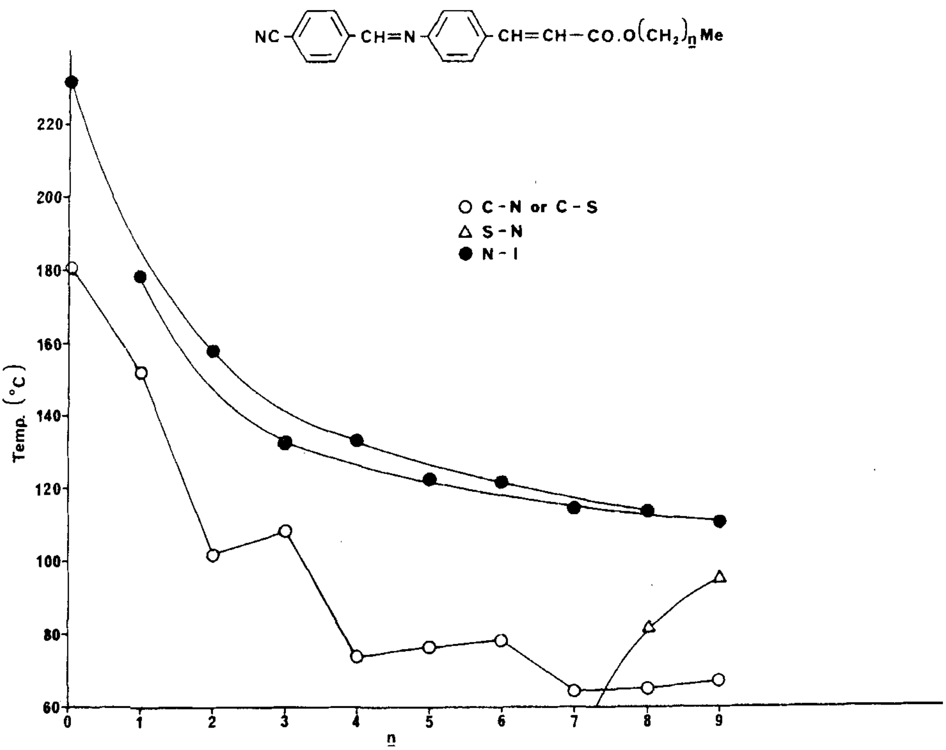


Figure 1. Plot of transition temperatures against number of methylene groups in the *n*-alkyl chain for the series of *n*-alkyl 4-*p*-cyanobenzylidene-aminocinnamates.

for the cyano-compounds; the two S–N temperatures lie on the first part of a steeply rising curve, and it is clear that higher members of the series would soon give purely smectic properties. For both series the melting points are fairly irregular, and this explains the absence of nematic properties for $X = NO_2$; R = ethyl. By extrapolating the appropriate curve, a predicted N–I temperature of *ca.* 140 °C is obtained for this ester. This is 37.5 °C below the melting point, and the isotropic liquid does not supercool to this degree.

Turning now to the *n*-alkyl esters with terminal substituent X = Ph, the transition temperatures are given in Table 3 and are plotted against the number of methylene groups in the *n*-alkyl group in Fig. 2. This series presents interesting features. It has already been shown(1) that a terminal phenyl group strongly promotes both smectic and nematic thermal stabilities, but it is clear from the results, particularly Fig. 2, that smectic properties are enhanced to the greater extent. Thus, only the first three esters show any nematic properties, and for the remainder of the series direct S–I transitions occur in the range 187–202 °C. In all cases, from the ethyl ester onwards, the crystals shrink markedly in the capillary at the temperatures denoted in Fig. 2 by open circles; further heating gives gradual changes, e.g., softening and some smearing, until a well defined change to a typically smectic state occurs at the temperatures denoted by full circles in Fig. 2. None of these changes is detectable with certainty by optical microscopy, and these esters must clearly

TABLE 3

System (I); X = Ph; Y = H

	Temperature (°C) of transition				
R = Alkyl	C–S_2(?)	C–S_1	S_2(?)–S_1	S_1–N	S_1 or N–I
Methyl	—	206	—	215.5	251.5
Ethyl	155	—	180	209	216
n-Propyl	125	—	169	205.5	210
n-Butyl	120	—	169.5	—	202
n-Pentyl	125	—	165.5	—	201
n-Hexyl	102	—	164	—	198
n-Heptyl	96	—	160	—	195
n-Octyl	105	—	159	—	192
n-Nonyl	95	—	156	—	189
n-Decyl	94	—	155	—	187

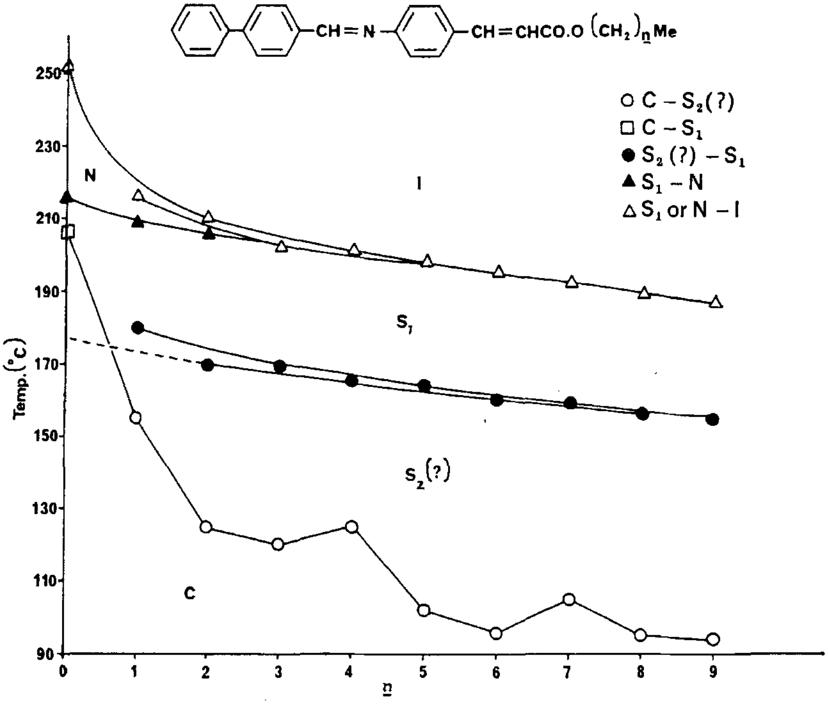


Figure 2. Plot of transition temperatures against number of methylene groups in the *n*-alkyl chain for the series of *n*-alkyl 4-*p*-phenylbenzylideneaminocinnamates.

be submitted to differential scanning calorimetry to establish more clearly the number and nature of the transitions occurring in this region.[†] Tentatively, the region between the open and the full circles in Fig. 2 has been designated smectic (S_2(?)), although more

[†] Since this paper was presented at the Berlin Conference, differential thermal analysis has been carried out on one of these esters, X = Ph, Y = H, R = ethyl. Although the results are of a preliminary nature, they show that only four transitions with measurable heat changes occur for this compound, and that they correspond to the transitions detected by melting point methods at 155°, 180°, 209° and 216 °C (Table 3). The largest heat change was associated with the lowest of these transitions, and moreover, this transition, *unlike the other three* was not precisely reversible on cooling, i.e., it occurred only after supercooling to 112 °C. This suggests that this transition at 155 °C does mark the change from the crystal to the smectic state rather than to some polymorphic crystal form. Since no detectable heat changes were noted between 155 °C and 180 °C, this indicates that only one smectic state (S_2) exists until 180 °C, when the second smectic form (S_1) is produced.

than one smectic state may occur in this region. The purity of the compounds is in no doubt and the changes observed in the capillary occur consistently and reproducibly over a range of heating rates. It is not felt therefore that the region in question relates to a spread melting point, and that the full circles represent the upper limits of C–S transitions. It is possible that the region denoted S_2(?) relates to one or more plastic, solid polymorphic modifications, but the regular trends in the temperatures denoted by full circles as the series is ascended suggest rather that these are temperatures at which mesomorphic–mesomorphic, i.e., S_2–S_1 changes are occurring. It is also significant that backward extrapolation of the lower S_2(?)–S_1 curve cuts the axis for $n = 0$, i.e., R = methyl, well below the melting point (C–S_1) for this ester. In fact, no anomalous melting process is observed for the methyl ester, and the S_2 state if it occurs is monotropic. Smooth curve relationships for smectic–smectic changes in homologous series have been recognized for many years,(6) but it is noted that these temperatures alternate for this series and that the alternation is the reverse of that for the N–I and S_1–I temperatures which also lie on two curves. The three S_1–N temperatures fit a short curve which merges with the N–I curves and would continue almost as the mean of the S_1–I curves. Further study is, however, clearly required to elucidate the phase transformations given by this series.

The transition temperatures for the systems (I) in which Y = H, R = n-alkyl and X = MeCO.O or MeO are summarized in Tables 4 and 5, respectively. Comparison of the results for the two series shows them to be broadly similar. The acetoxy group clearly stabilizes both smectic and nematic states relative to methoxy, the smectic state being stabilized to the greater degree for most of the homologues. The result is that the acetoxy compound with R = n-decyl is purely smectic, and for the methoxy compounds, the methyl ester is purely nematic. Polymesomorphism of the smectic state occurs to a minor degree when X = MeO; the smectic states, S_2, are monotropic.

Figures 3 and 4 represent the plots of the transition temperatures against the number of methylene groups in the alkyl groups for the series of acetoxy and methoxy substituted esters, respectively.

The melting points and N–I temperatures reveal no unusual features, but the S–N temperatures are quite unusual in their trends. For both series, these temperatures clearly alternate, whereas S–N temperatures for homologous series normally fit one curve which rises steeply at first, then levels off and becomes coincident with the falling N–I curve.⁽⁷⁾ For the methoxy compounds (Fig. 4), both curves, the upper of which is for *n*-alkyl esters with an even number of carbon atoms in the chain, fall to a shallow minimum then rise and

TABLE 4
System (I); X = MeCO.O; Y = H

	Temperature (°C) of transition			
R = Alkyl	C–S	S–N	N–I	S–I
Methyl	136.5	139.5	198	—
Ethyl	106.5	124.5	155	—
n-Propyl	114.5	122.5	149	—
n-Butyl	80.5	107	122	—
n-Pentyl	81	104.5	125	—
n-Hexyl	53.5	105.5	115.5	—
n-Heptyl	66	105	114.5	—
n-Octyl	62.5	110	113.5	—
n-Nonyl	73	111.5	113	—
n-Decyl	70.5	—	—	113

TABLE 5
System (I); X = MeO; Y = H

	Temperature (°C) of transition				
R = Alkyl	C–N	C–S_1	S_2–S_1	S_1–N	N–I
Methyl	160.5	—	—	—	180.5
Ethyl	—	109	—	118.5	140
n-Propyl	—	79.5	—	98.5	132
n-Butyl	—	71	—	95	111.5
n-Pentyl	—	70	—	88.5	115
n-Hexyl	—	62	—	89.5	105.5
n-Heptyl	—	63.5	—	91	107
n-Octyl	—	57.5	—	94.5	101.5
n-Nonyl	—	61	($<$ 40)†	97	102
n-Decyl	—	64.5	($<$ 40)†	98.5	100

† Monotropic smectic—smectic transitions. The mesophases are observed only on rapidly chilling the sample, and with a rate of cooling commensurate with measuring accurate temperatures, crystallisation occurred at the temperatures indicated.

merge, but do not quite join the N–I curves even for the *n*-decyl ester. We have already noted that the terminal MeO group stabilizes smectic less than nematic states relative to the terminal MeCO.O group. Thus, for the acetoxy series, smectic properties arise earlier in the series and nematic properties are extinguished earlier in the series. As a result, more of the S–N curves is seen (Fig. 3). The curve for the even homologues is similar to that for the methoxy compounds, but that for the odd homologues falls gradually at first, then more steeply before reaching its shallow minimum and rising again. Moreover, the two curves cross at about their minima. Neither the alternation of these S–N temperatures nor the shapes of the curves to which they give rise can yet be explained. Apparently however, the forces maintaining order in these smectic states are susceptible to odd–even changes in the nature of the alkyl group.

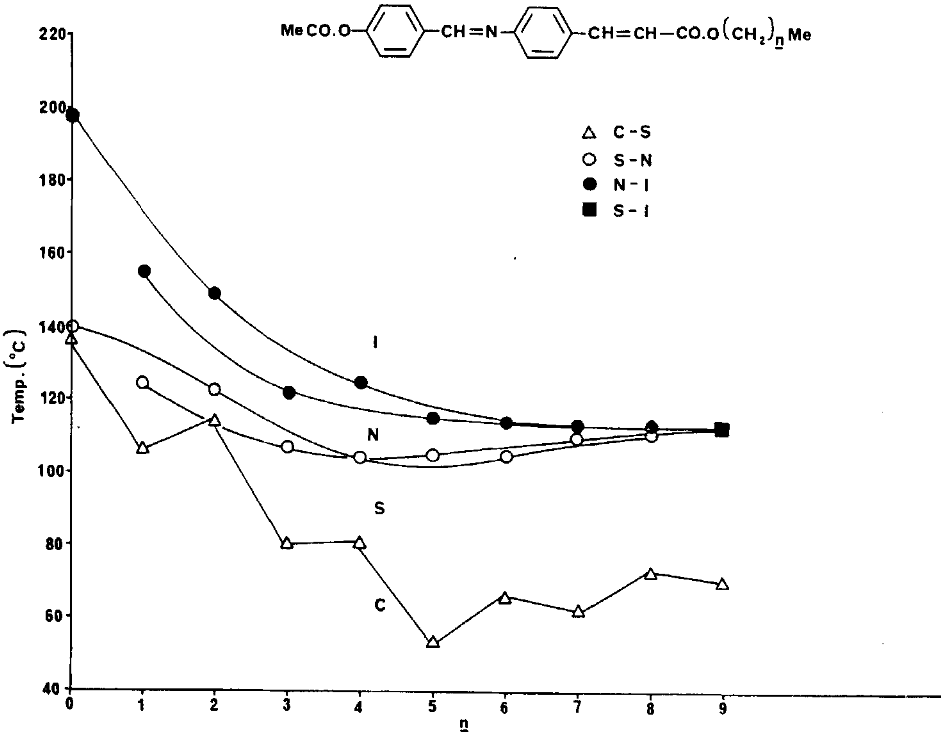


Figure 3. Plot of transition temperatures against number of methylene groups in the *n*-alkyl chain for the series of *n*-alkyl 4-*p*-acetoxybenzylideneaminocinnamates.

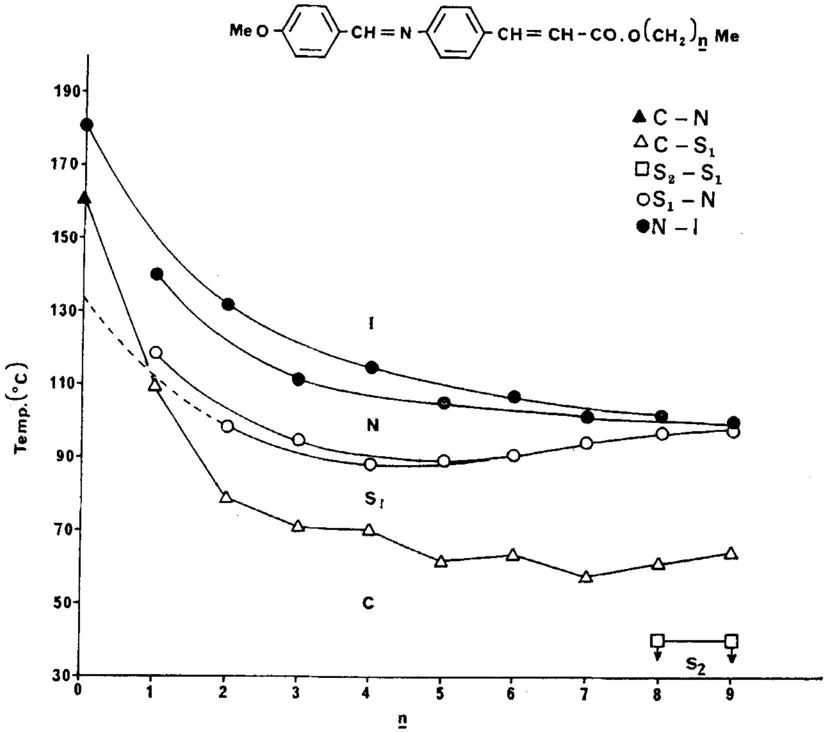


Figure 4. Plot of transition temperatures against number of methylene groups in the *n*-alkyl chain for the series of *n*-alkyl 4-*p*-methoxybenzylidene-aminocinnamates.

The shapes of the curves also add further types to the already considerable number of smooth curve relationships already established(7) for homologous series. These facts suggest that an understanding of the S–N transition may be less easy to achieve than might have been anticipated.

Before leaving these series of *n*-alkyl esters, three further points may be made.

(1) Because of the marked smectogenic tendencies of the system with X = Ph, and the marked nematogenic tendencies of the system with X = CN or NO_2, comparisons of the orders of terminal efficiency of the groups X on smectic *and* nematic states for all five systems are not easily made. Considering the *n*-propyl esters, the nematic terminal group efficiency order is

$$\mathrm{Ph} \gg \mathrm{CN} > \mathrm{MeCO.O} > \mathrm{NO_2} > \mathrm{MeO},$$

but if comparisons are made for the *n*-pentyl or higher esters, the positions of NO_2 and MeO are reversed.

For all homologues, the smectic terminal group efficiency order is

$$\text{Ph} \gg \text{MeCO.O} > \text{MeO}.$$

If the *n*-decyl esters are considered, the smectic cyano-compound may be included in the order which becomes

$$\text{Ph} \gg \text{MeCO.O} > \text{MeO} > \text{CN} > \text{NO}_2;$$

the nitro-compound is not in fact smectic, but the C–N temperature is lower than the S–N temperature of the cyano-decyl ester. Therefore, if the nitro-compound did give a smectic state, it would be the least stable of the set.

These efficiency orders agree with more extensive orders reported elsewhere.(1,8)

(2) As mentioned already, none of the esters in the five series is particularly low melting, the lowest being with $X = \text{MeCO.O}$ and $R = n$-hexyl, the compound having constants C–S, 53.5°; S–N, 105.5°; N–I, 115.5 °C. The lowest melting, purely nematic compound was that with $X = \text{CN}$ and $R = n$-octyl; the constants were C–N, 64°; N–I, 114.5 °C.

Compounds of structure (I), with $Y = \text{Me}$, reported in the literature(9) are apparently less smectogenic, but the effect of the methyl group on melting point is unpredictable. We find that when $X = \text{CN}$, the effect of changing Y from H to Me always raises the melting point. With $X = \text{MeCO.O}$ or MeO, melting point decreases were however obtained, and moreover, the α-methyl group decreased smectic more than nematic thermal stabilities. Some lower melting, purely nematic systems were thus obtained, e.g.,

$X = \text{MeO}$; $Y = \text{Me}$; $R = n$-octyl C–N, 49.5°; N–I, 52.5 °C,
compared with
$X = \text{MeO}$; $Y = \text{H}$; $R = n$-octyl C–S, 57.5°; S–N, 94.5°; N–I, 101.5 °C.

For two of the compounds with $Y = \text{Me}$ we obtained different constants to those listed by Kast.(9) For $X = \text{MeO}$; $Y = \text{Me}$; $R = n$-butyl we found: C–N, 52.5°; N–I, 61.5 °C. Kast lists a monotropic liquid crystal, the compound having a C–I transition at 58 °C. For $X = \text{MeO}$; $Y = \text{Me}$; $R = n$-propyl we found: C–N, 69.5°; N–I, 91.5 °C. Kast lists C–N, 50°; N–I, 85 °C. Recently Leclerq *et al.*⁽³⁾ reported the following constants for this ester: C–N, 67.5°; N–I, 83.5 °C, agreeing closely with our melting point, but giving a considerably lower N–I temperature. This propyl ester has attracted some interest because the nematic state supercools readily to room temperature. The tendency of the supercooled melt to crystallize diminishes with the number of times the sample is heated. Eventually, amorphous isotropic areas become obvious in the nematic state even at room temperature, and we have shown by infra-red spectroscopy that on heating at 75 °C, breakdown of the Schiff's base occurs and generates the free amine. The decomposition is slow, but none the less significant. On rather limited data, it appears that thermal decomposition of such Schiff's bases is much *less* marked when $Y = \mathrm{H}$. For these reasons, we now avoid heating Schiff's bases in which $Y = \mathrm{Me}$ during their preparation and, as far as possible, in their subsequent purification. For the propyl ester under discussion, these precautions may account for the higher constants compared with those given by Leclerq *et al.*⁽³⁾

(3) One example of the type of polymorphic behaviour which may be encountered with Schiff's bases of structure (I) is now quoted. Consider the system $X = \mathrm{CN}$; $Y = \mathrm{H}$; $R = n$-butyl. The crystalline material obtained from organic solvents gives the following constants: C–N, 108.5°; N–I, 132.5 °C, but some softening of the crystals was observed at 90 °C. The sample had not decomposed, and later, by hot stage microscopy, it was established that two distinct polymorphic forms of the solid exist, these having different melting points. When the amorphous isotropic liquid is cooled the nematic phase forms and crystallizes as a mixture of solids (C_1 and C_2). On reheating, the solids melt at their respective melting points. On standing in the cold, C_2 reverts slowly to C_1. The situation is summarized below:

$$\begin{tikzcd}
C_2 \arrow[r, shift left, "108.5^\circ"] \arrow[dr, "\text{slowly in the cold}"'] & N \arrow[l, shift left] \arrow[r, shift left, "132.5^\circ"] \arrow[d, shift right] & I \arrow[l, shift left] \\
& C_1 \arrow[u, shift right, "90^\circ"'] &
\end{tikzcd}$$

These results agree well with the observations of Leclerq *et al.*⁽³⁾ on this compound: they quote C–N, 87°; N–I, 133 °C and comment that on first melting the crystalline material the C–N change occurs at 108 °C.

SYSTEMS OF STRUCTURE (I); $Y = H$; R = A BRANCHED ALKYL GROUP

The effects of chain branching of the ester alkyl group R in system (I) were now examined, and Tables 6, 7 and 8 summarize some of the results. Compounds with X = CN and X = Ph have been chosen to show the effects of branching on nematic and smectic thermal stabilities, respectively. Considering the data in Table 6, movement of the methyl group from carbon_1 to carbon_2 of the *n*-pentyl chain has the following results. The 1-methyl group eliminates nematic properties and a dramatic decrease in N–I temperature of > 113 °C is involved. The 2-methyl group then raises the N–I temperature again, and so also do 3- or 4-methyl groups, but none of the branched chain esters attains a N–I temperature as high as the *n*-pentyl ester. With X = Ph, the largest decrease in S–I temperature is again found with 1-methyl substitution, but now the decrease is only 21 °C. Thereafter, 2-, 3- and 4-methyl substitution gradually increase the S–I temperatures, finally to within 2.5 °C of the *n*-pentyl ester.

As shown by the results in Tables 7 and 8, similar effects are observed for the branched chain pentyl, butyl and propyl esters.

TABLE 6

System (I); X = CN or Ph; Y = H

	X = CN		X = Ph	
R	C–N or I (°C)	N–I (°C)	C–S (°C)	S–I (°C)
$—CH_2CH_2CH_2CH_2Me$	74	133	165.5	201
$—CHMeCH_2CH_2CH_2Me$	61.5	(< 20)†	169.5	180
$—CH_2CHMeCH_2CH_2Me$	90	107.5	156	187
$—CH_2CH_2CHMeCH_2Me$	81.5	101.5	165	194.5
$—CH_2CH_2CH_2CHMe_2$	67.5	116.5	168.5	198.5

† No nematic state was in fact detected even on rapid chilling. The temperature is recorded merely to indicate the extent to which the isotropic liquid could be supercooled, at moderate cooling rates, before crystallisation occurred, and to illustrate as far as possible how much the thermal stability of the nematic state of the parent compound has been affected by the structural change.

TABLE 7
System (I); X = CN or Ph; Y = H

	X = CN		X = Ph	
R	C–N or I (°C)	N–I (°C)	C–S (°C)	S–I (°C)
—CH$_2$CH$_2$CH$_2$Me	108.5	132.5	169.5	202
—CHMeCH$_2$CH$_2$Me	73.5	(< 63)†	172.5	185
—CH$_2$CHMeCH$_2$Me	93.5	108	161	194.5
—CH$_2$CH$_2$CHMe$_2$	101	107	169.5	200.5

† The temperature in parenthesis is for a monotropic transition. The mesophase is observed only on rapidly chilling the sample, and with a rate of cooling commensurate with measuring accurate temperatures, crystallisation occurred at the temperature indicated.

TABLE 8
System (I); X = CN or Ph; Y = H

	X = CN		X = Ph			
R	C–N or I (°C)	N–I (°C)	C–S (°C)	S–N (°C)	S–I (°C)	N–I (°C)
—CH$_2$Me	152	178.5	180	209	—	216
—CHMe$_2$	140	($\leqslant$127)†	171‡	—	198	—
—CH$_2$CH$_2$Me	102	158	169	205.5	—	210
—CHMeCH$_2$Me	111	(<89)§	172	—	189.5	—
—CH$_2$CHMe$_2$	127	139	160	202	—	209.5

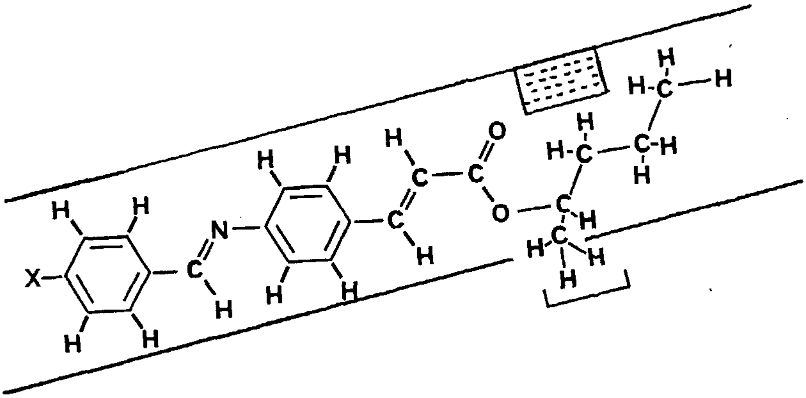
† No nematic state was in fact detected even on rapid chilling. The temperature is recorded merely to indicate the extent to which the isotropic liquid could be supercooled, at moderate cooling rates, before crystallisation occurred, and to illustrate as far as possible how much the thermal stability of the nematic state of the parent compound has been affected by the structural change.

‡ Two smectic states detected (S$_2$–S$_1$, 178 °C).

§ The mesophase is observed only on rapidly chilling the sample, and with a rate of cooling commensurate with measuring accurate temperatures, crystallisation occurred at the temperature indicated.

The trends in the results in Table 7 are self evident as are those in Table 8 for X = CN. For X = Ph (Table 8), the 1-methyl group of the isopropyl ester converts the smectic/nematic ethyl ester into a purely smectic ester with a lower S–I temperature. A similar change occurs on passing from the *n*-propyl to the 1-methylpropyl ester with X = Ph, whilst the 2-methylpropyl ester regains nematic thermal stability to a large extent, and the S–N temperature is 3.5 °C lower than for the *n*-propyl ester.

Since the effect of chain branching on both types of liquid crystal becomes less marked as the point of branching is moved to the extremity of the alkyl chain, this suggests that intramolecular steric effects may be operating. In order to minimize steric interference with the oxygen of the carbonyl group, a 1-methyl substituent in the chain is most likely to lie as shown in structure (II). The protruding methyl group should force the long axes of the molecules apart, but it is suggested that in these systems the effect is greater in the nematic state in which separation must be adequate to permit the molecules to slide past one another in the direction of their long axes. In the layer arrangement of the smectic state, the 1-methyl group may be partially accommodated in the shaded area of a neighbouring molecule in the layer. Movement of the methyl group to carbon$_2$ allows the group to be accommodated, partially at least, within the shaded area of its own molecule with less dramatic effects on smectic and particularly nematic properties. These proposals are reminiscent of those made concerning the effects of gap-filling substituents in 5-substituted-6-*n*-alkoxy-2-naphthoic acids and other systems,$^{(1)}$ and at first sight the *smectic* thermal stabilities of the 1-methyl substituted systems and possibly the nematic and smectic thermal stabilities of the 2-methyl substituted systems might be expected to be higher than those for the *n*-alkyl ester. However, such chain branching methyl groups also thicken the molecules, and this may counteract these effects giving the small nett decreases observed.



II

Movement of the point of branching towards the extremities of the chain has quite small effects, and it is suggested that the increasing number of flexible methylene units between the CO.O function and the point of branching allows the alkyl group to assume some conformation such that the broadening and thickening effects are minimal.

These proposals are qualitative and tentative, but they are supported to some extent by the fact that preliminary studies(10) of chain branching of alkyl groups of the ether function indicate that a methyl branch at carbon_1 has similar, moderate effects on *both* smectic and nematic thermal stabilities. In this different chemical environment, intramolecular steric effects of the type discussed above and assumed responsible for the effects of chain branching in the esters cannot arise.

LIQUID CRYSTALLINE PROPERTIES OF ω-SUBSTITUTED n-ALKYL ESTERS OF SYSTEM (I)

The regular changes which are observed in liquid crystal transition temperatures on ascending homologous series of the type discussed here and in other places suggests that, in these systems at least, the n-alkyl chains adopt extended conformations such that successive methylene units give rise to regular changes in the intermolecular forces, leading to regular alternation and smooth curve relationships for the transition temperatures of the series. The possible influence of intermolecular contacts between terminal methyl groups(8) of even and odd n-alkyl chains has been proposed as a possible explanation of the alternation of liquid crystal-isotropic temperatures, and it was felt to be of interest to examine the effects of other terminal groups in a polymethylene chain. Esters of the following type were therefore studied:

System (I); $Y = \text{H}$

(a) $X = \text{CN, Ph or MeO}$; $R = (\text{CH}_2)_n\text{Ph}$ ($n = 0-4$)
(b) $X = \text{CN or MeCO.O}$; $R = (\text{CH}_2)_n\text{CHMe}_2$ ($n = 0-3$).

The terminal methyl group of the n-alkyl chain is therefore replaced by Ph or CHMe_2. The transition temperatures for these systems are given in Tables 9 and 10.

TABLE 9

System (I); X = CN, Ph or MeO; Y = H; R = $(CH_2)_n$Ph

	X = CN		X = Ph				X = MeO			
n	C–N or I (°C)	N–I (°C)	C–S or I (°C)	S–N (°C)	S–I (°C)	N–I (°C)	C–N or I (°C)	S–N (°C)	S–I (°C)	N–I (°C)
0	168	277	183	185.5	—	> 240	135.5	(124)	—	240
1	160	(87)	189	—	(178.5)	—	123	—	(<70)	—
2	145.5	185.5	169.5	179.5	—	217	152.5	(<90)	—	(148)
3	97	(48.5)	160	—	164.5	—	103.5	—	(65)	—
4	119.5	127	152	168.5	—	173	100.5	(56)	—	(99.5)

Monotropic transition temperatures are in parenthesis. Where such a temperature is preceded by <, this means that the mesophase is observed only on rapidly chilling the sample, and that with a rate of cooling commensurate with measuring accurate temperatures, crystallisation occurred at the temperatures indicated.

TABLE 10

System (I); X = CN or MeCO.O; Y = H; $R = (CH_2)_nCHMe_2$

	X = CN		X = MeCO.O			
n	C–N or I (°C)	N–I (°C)	C–S (°C)	S–N (°C)	S–I (°C)	N–I (°C)
0	140	(< 130)†	80	—	107	—
1	127	139	104.5	111.5	—	143
2	101	107	75.5	—	110.5	—
3	67.5	116.5	87	108.5	—	114

† No nematic state was in fact detected even on rapid chilling. The temperature is recorded merely to indicate the extent to which the isotropic liquid could be supercooled, at moderate cooling rates, before crystallisation occurred, and to illustrate as far as possible how much the thermal stability of the nematic state has been affected.

The general point is made first that smectic properties occur in the systems with X = Ph, MeCO.O or MeO, i.e., with terminal groups which favour nematic less than smectic properties. Irrespective of X, there is however, a marked alternation in the nematic tendencies for both types of ester as n is increased. This is manifested in one of two ways:

(1) by a high alternation of the N–I temperatures—this is shown clearly in Fig. 5, a plot of transition temperatures for system (I), X = CN; Y = H; $R = (CH_2)_nPh$ against n;

(2) by an alternation between (a) smectic and (b) smectic/nematic behaviour—this is illustrated in Fig. 6, a plot of transition temperatures for system (I), X = Ph; Y = H; $R = (CH_2)_nPh$ against n. In such cases, the N–I temperatures must alternate to an extent such that the nematic states become meta-stable relative to the smectic states and fail to appear in alternate members of the series, so giving alternate purely smectic systems.

Where observed, the S–N and S–I temperatures also alternate as n is increased, but much less markedly. In fact for system (I), X = MeCO.O; Y = H; $R = (CH_2)_nCHMe_2$, the alternation is negligible, and the S–N and S–I temperatures fit a single curve when plotted against n—see Fig. 7.

A study of molecular models reveals a possible explanation of these results. Assuming that the methylene chain adopts a zig-zag conformation perpetuating the major axis of the molecule, when n is odd

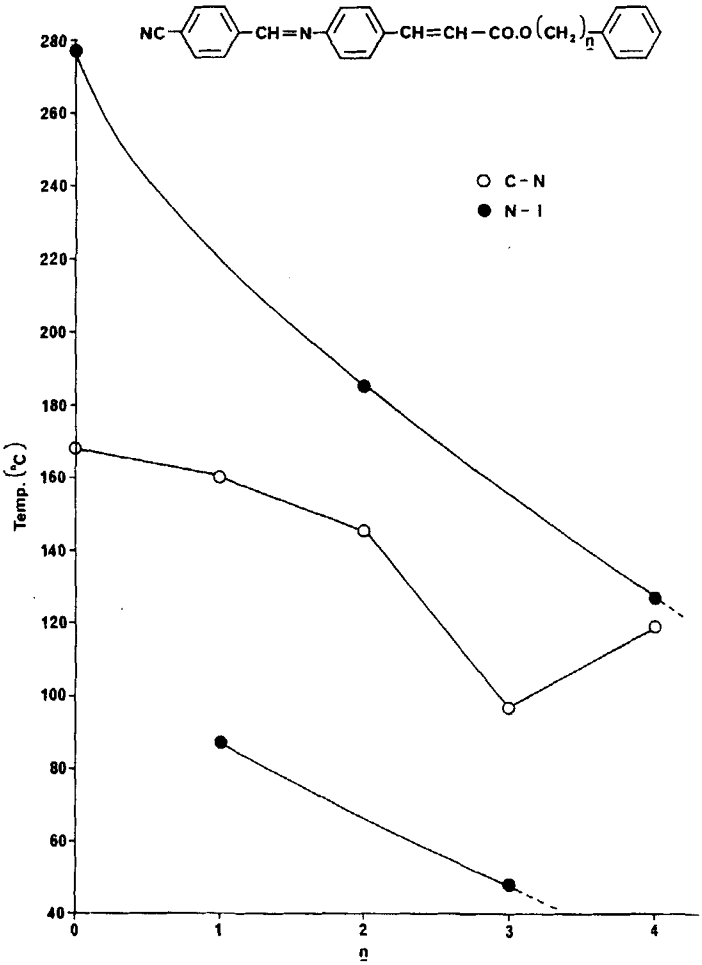


Figure 5. Plot of transition temperatures against number of methylene groups (n) in the chain of ω-phenylalkyl 4-p-cyanobenzylideneaminocinnamates.

for $(CH_2)_nPh$ and even for $(CH_2)_nCHMe_2$, the terminal Ph and Me groups respectively project beyond a line defining the perimeter of the rest of the molecule. In fact, the long axes of the molecules bend over slightly at their extremities and the molecules may be represented in an exaggerated way as in Fig. 8a. Although a smectic layer comprised of such molecules may be stable, the side spacing of the molecules in the nematic state to which this layer may give rise will

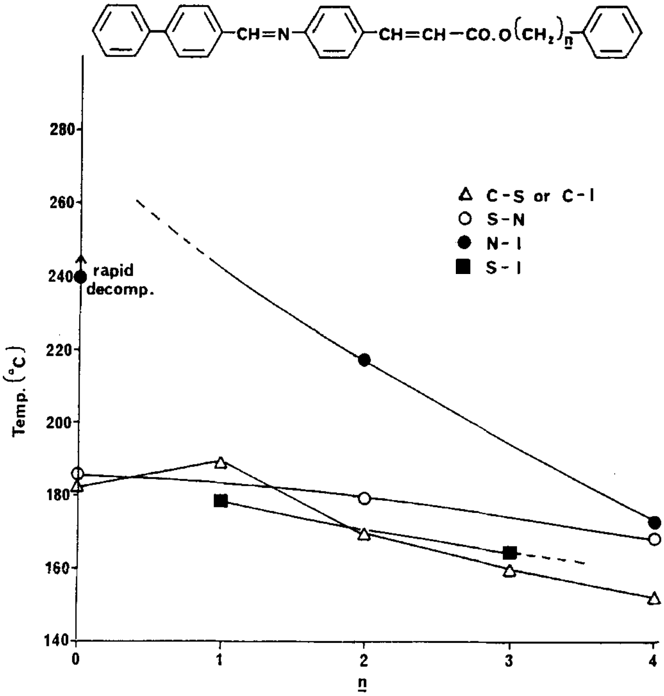


Figure 6. Plot of transition temperatures against number of methylene groups (n) in the chain of ω-phenylalkyl 4-p-phenylbenzylideneaminocinnamates.

be much greater than that in a nematic state comprised of simple, linear rod-like molecules (Fig. 8b), as is the situation for esters with $R = (CH_2)_nPh$ when n is even or $R = (CH_2)_nCHMe_2$ when n is odd. The thermal stability of a nematic state as depicted in Fig. 8a could be so low that a direct S–I transition occurs on heating, as is observed with the compounds in Tables 9 and 10 when X = Ph, MeO and MeCO.O. Only with X = CN, a group strongly favouring nematic properties, do esters with $R = (CH_2)_nPh$, when n is odd, and $R = (CH_2)_nCHMe_2$, when n is even, give nematic states. In these cases, the N–I temperatures are markedly lower than for the related esters for which n is even and odd, respectively. As would be expected, the alternation is greater for $(CH_2)_nPh$ than for $(CH_2)_nCHMe_2$, where the protruding Me group is smaller, and in all cases the degree of alternation decreases quickly with increasing number of methylene units, the greater length of flexible alkyl chain presumably allowing

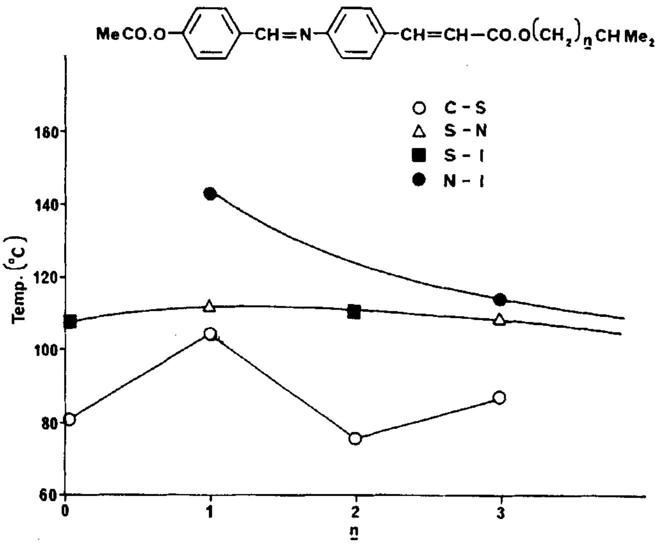


Figure 7. Plot of transition temperatures against number of methylene groups (n) in the chain of ω-isopropylalkyl 4-p-acetoxybenzylideneamino-cinnamates.

a more similar conformation to be adopted by odd and even chain members.

Similar results(10) have also been obtained for ω-cyclohexylalkyl esters: system (I); X = Ph, CN or NO_2; Y = H; R = $(CH_2)_nC_6H_{11}$ – $n = 0 - 2$. Since the cyclohexyl group is bulky, the N–I temperatures again alternate markedly for the purely nematic esters with X = CN or NO_2; the esters for which X = Ph are purely smectic, the S–I temperatures alternating only moderately.

Such results are also reminiscent of those obtained by Ennulat(11) with cholesteryl and thiocholesteryl ω-phenylalkanoates for which Ch–I temperatures alternate profoundly; see also the Proceedings of the Third International Liquid Crystal Conference, Berlin, 1970, for further developments of this work.

In conclusion, it is interesting to note that in certain esters involving R groups $(CH_2)_nPh$ and $(CH_2)_nCHMe_2$ and also in those involving branching of a n-alkyl chain at carbon$_1$, it has been suggested that a group projecting beyond the perimeter of the rest of the molecule is responsible for dramatic changes in nematic thermal stability and more minor changes in smectic thermal stability. In these cases, the

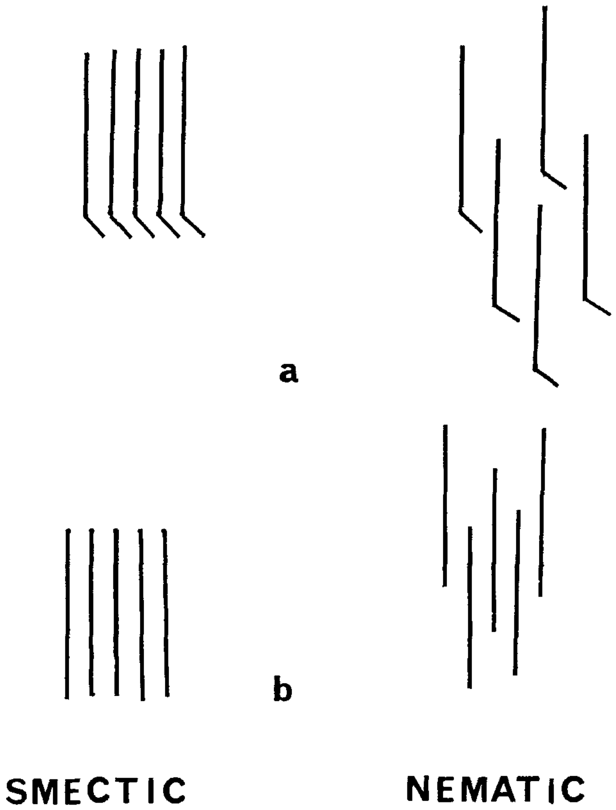


Figure 8. Representation of the arrangement of (a) terminally branched (b) linear rod-like molecules in a smectic layer and the nematic state.

projection occurs either at a point where a gap in a neighbouring molecule exists or at the extremity of the molecule. The consequences have therefore been quite different to those in cases in which substituents are introduced into rigid core parts of the molecules, e.g., into aromatic rings, when the relative effects on smectic and nematic thermal stabilities are dependent on size and polarity of the substituent.(8)

2. Materials and Methods

Full details of the preparation and purification of the Schiff's bases will be published elsewhere. Standard methods of synthesis have, however, been employed generally and all intermediate and final products have been checked for purity by as wide a range of techniques as was practicable: combustion analysis, gas-liquid chromatography, thin-layer chromatography, mass spectrometry, infra-red spectroscopy, nuclear magnetic resonance spectroscopy.

Hot stage optical microscopy was carried out with equipment supplied by C. Reichert, Optische Werke A.G., Wien, Austria.

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