

CHAPTER II

SYNTHESIS AND MESOMORPHIC PROPERTIES OF TRANS-p-n- ALKOXY- α -METHYLCINNAMIC ACIDS AND THEIR ESTERS WITH p-HYDROXYBENZONITRILE

2.1 Survey of the mesomorphic properties of substituted cinnamic acids

Many homologous series of compounds involving cinnamic acid moiety have been reported in the literature.¹⁻⁷ Bennet and Jones¹ synthesised a homologous series of trans-p-n-alkoxycinnamic acids and compared the variation in the mesomorphic properties with a series of p-n-alkoxybenzoic acids. They concluded that the range of the mesophase is generally wider in the benzoic acid series as compared with the cinnamic acid series. On the other hand, because of increased anisotropy of polarisability due to the double bond, the mesophase of cinnamic acids would be expected to have higher thermal stabilities. Indeed, the cinnamic acids do have higher thermal stabilities than those for benzoic acids. However, the relatively high melting points of the cinnamic acids would cut off, as it were, the lower region of possible existence of mesophases of these substances, thus lowering the range. Later Gray and Jones² synthesised the same trans-p-n-alkoxycinnamic acids to compare the mesomorphic properties with those exhibited by 6-n-alkoxy-2-naphthoic

acids. Gray and Jones² found substantial variation in the transition temperatures from those obtained by Bennet and Jones and have attributed this to the greater purity of the compounds prepared by the former. Later Gray *et al*³ studied the mesomorphic properties of trans-4-n-alkoxy-3-halogenocinnamic acids. This halogen substitution increases the breadth and polarisability of the trans-n-n-alkoxycinnamic acids, which in turn would alter the thermal stabilities of the mesophases. In fact, Gray⁸ has studied the effect of introducing various substituents on the mesophases formed by several systems. Also, it is known⁹⁻¹⁶ that, when compared with the unsubstituted parent compounds, lateral substituents, either at the ortho position on a phenyl ring or the α -position of a central linkage group will reduce both the solid-mesophase and mesophase-isotropic transition temperatures, the latter however, being more marked. The extent of reduction of the temperature depends on the size of the lateral substituent and the shape of the substituted molecule.

During the last few years much attention has been paid to the synthesis of new liquid crystalline compounds of low melting points and suitable nematic ranges and other physical parameters. Jones and Ratto¹⁷⁻¹⁹ have reported a number of derivatives of cinnamic acid with fairly low melting points and wide thermal ranges. The interest in the present study was (i) to examine the effect of an α -methyl

substituent on the mesomorphic properties of some para-substituted cinnamic acids, and (ii) to prepare a number of low-melting materials with high positive dielectric anisotropy for possible use in display applications.

2.2 trans-p-n-Alkoxy- α -methylcinnamic acids: Preparation and properties

These acids were conveniently prepared by heating a mixture of an appropriate aldehyde, propionic anhydride and potassium propionate following the procedure of Johnson²⁰ (Chart I). Carboxylic acids in general, exist in the form of dimers. Only linear dimers show mesomorphic properties if they also have other requisites of a potential mesogenic compound. For example, a cis-p-n-alkoxycinnamic acid, Fig. 2.1a forms a dimer, but the dimer is not linear and consequently it is not mesomorphic. A trans-p-n-alkoxycinnamic acid, Fig. 2.1b forms a linear dimer and therefore is mesomorphic. The linear dimeric form of trans-p-n-alkoxy- α -methylcinnamic acid is shown in Fig. 2.1c.

The transition temperatures of the parent compounds are given in table 2.1 and those for trans-p-n-alkoxy- α -methylcinnamic acids are summarised in table 2.2. The p-methoxy and p-ethoxy derivatives are non-mesomorphic. This is due to their high melting points and the thermal energy will be too much for the molecules to retain any

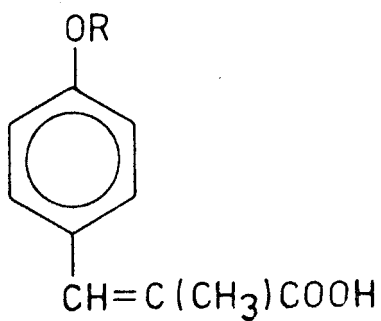
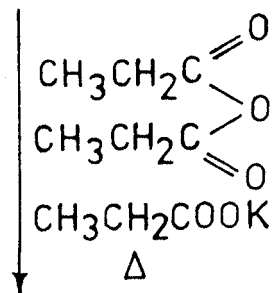
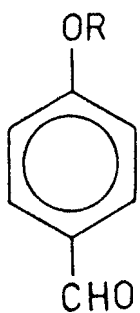
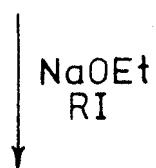
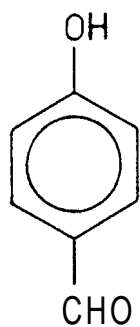
substituent on the mesomorphic properties of some para-substituted cinnamic acids, and (&&) @ prepare a number of low-melting materials with high positive dielectric anisotropy for possible use in display applications.

2.2 trans-p-n-Alkoxy- α -methylcinnamic acids: Preparation and properties

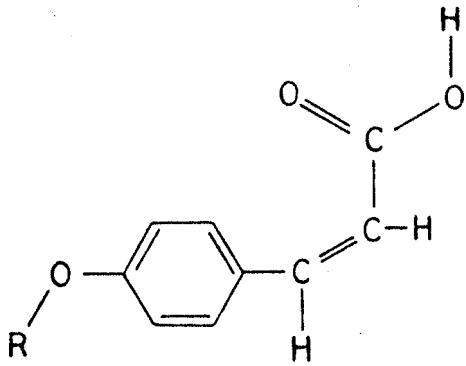
These acids were conveniently prepared by heating a mixture of an appropriate aldehyde, propionic anhydride and potassium propionate following the procedure of Johnson²⁰ (Chart I). Carboxylic acids in general, exist in the form of dimers. Only linear dimers show mesomorphic properties if they also have other requisites of a potential mesogenic compound. For example, a cis-p-n-alkoxycinnamic acid, Fig. 2.1a forms a dimer, but the dimer is not linear and consequently it is not mesomorphic. A trans-p-n-alkoxycinnamic acid, Fig. 2.1b forms a linear dimer and therefore is mesomorphic. The linear dimeric form of trans-p-n-alkoxy- α -methylcinnamic acid is shown in Fig.2.1c.

The transition temperatures of the parent compounds are given in table 2.1 and those for trans-p-n-alkoxy- α -methylcinnamic acids are summarised in table 2.2. The p-methoxy and p-ethoxy derivatives are non-mesomorphic. This is due to their high melting points and the thermal energy will be too much for the molecules to retain any

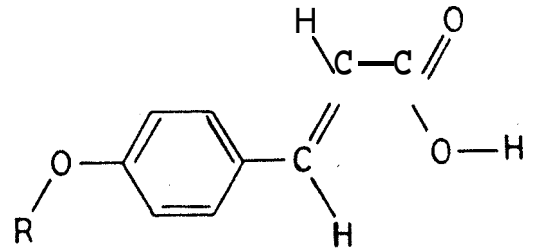
CHART I



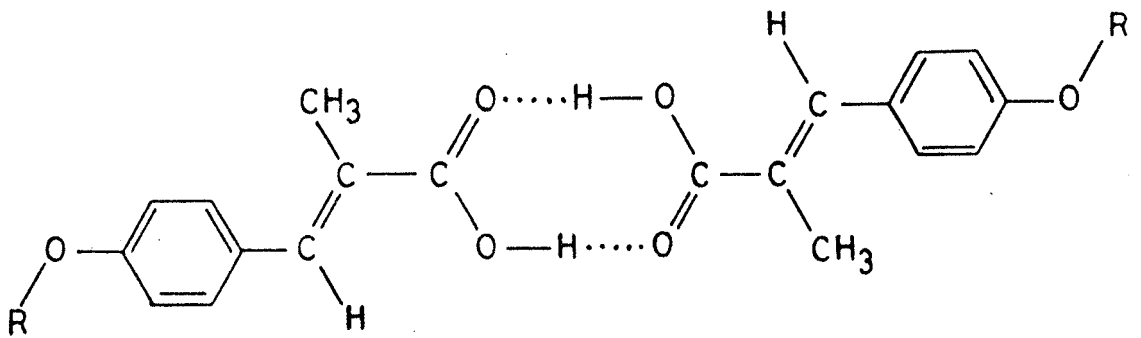
R = n-Alkyl



(a)



(b)



R = n-Alkyl

(c)

Figure 2.1: Molecular structures of (a) cis-p-n-alkoxy-cinnamic acid (b) trans-p-n-alkoxycinnamic acid (c) dimeric form of trans-p-n-alkoxy- α -methylcinnamic acid.

Table 2.1

Transition temperatures of trans-p-n-alkoxy-
 cinnamic acids,² $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}=\text{CH}\cdot\text{COOH}$

Compound number	R = n-Alkyl	Temperature transition to			ΔT , °C Nematic range
		Smectic, °C	Nematic, °C	Isotropic, °C	
1	CH ₃	-	173.5	190	16.5
2	C ₂ H ₅	-	194	198.5	4.5
3	C ₃ H ₇	-	167	184.5	17.5
4	C ₄ H ₉	-	156	189.5	33.5
5	C ₅ H ₁₁	-	139.5	179.5	40
6	C ₆ H ₁₃	-	153	181.5	28.5
7	C ₇ H ₁₅	-	148	175	27
8	C ₈ H ₁₇	-	146	174.5	28.5
9	C ₉ H ₁₉	138.5	144	171	27
10	C ₁₀ H ₂₁	136	150.5	169	18.5
11	C ₁₂ H ₂₅	132	157	165	8

Table 2.2

Transition temperatures of trans-p-n-alkoxy- α -methyl-
 cinnamic acids, $RO.C_6H_4.CH=C(CH_3).COOH$

Compound number	R=n-Alkyl	Temperature of transition to		ΔT , °C Nematic Range
		Nematic, °C	Isotropic, °C	
1	CH ₃	-	153	-
2	C ₂ H ₅	-	167	-
3	C ₃ H ₇	130.1	138.2	8.1
4	C ₄ H ₉	110	143	33
5	C ₅ H ₁₁	97	132	35
6	C ₆ H ₁₃	102	131.7	29.7
7	C ₇ H ₁₅	93	120.5	27.5
8	C ₈ H ₁₇	83	123	40
9	C ₉ H ₁₉	82.5	117.5	35
10	C ₁₀ H ₂₁	79.5	116.5	37
11	C ₁₁ H ₂₃	88.2	112.5	24.3
12	C ₁₂ H ₂₅	86	111.5	25.5

ordered arrangement. Moreover, the isotropic liquids of these two compounds do not sufficiently supercool for a monotropic nematic phase to be obtained. The α -methyl group of the central linkage has a pronounced effect on the types as well as transition temperatures of the mesophases, when compared with those of the unsubstituted parent compounds. It is apparent from tables 2.1 and 2.2 that, there is a marked decrease in the melting points ($\sim 40-50^\circ$) and moreover the homologues 3 to 12 are purely nematic, the smectic phase having been altogether eliminated. This trend is in accordance with the work of Gray and co-workers²¹ on various mesomorphic homologous series of compounds, which show a similar behaviour. Even though the clearing points have also decreased in the substituted compounds (see tables 2.1 and 2.2) in most cases, the thermal range of the nematic phase has increased for the higher homologues as a result of introduction of the α -methyl group.

The reduction in transition temperatures may be explained as follows. A construction of the Dreiding model of this acid shows that there is no substantial broadening due to the α -methyl substituent. The α -methyl group causes a thickening effect which is considerably enhanced due to a steric effect between the methyl group and the ortho ring protons. This leads to an interference with the close packing of the molecules, increase the molecular separation

and thereby reducing the strength of the intermolecular attractions.

Figure 2.2 shows a plot of the transition temperatures against the number of carbon atoms in the alkoxy chain. The general trend that has been observed by a number of workers in the field is that T_{N-I} decreases in ascending the series. It is seen that for these compounds the T_{N-I} points lie on two smooth falling curves. The curve for the even homologues lies above that for the odd ones. A similar trend has been observed for the unsubstituted parent homologues synthesised by Gray and Jones.² In the unsubstituted series, trans-p-n-nonyloxycinamic acid exhibits a smectic phase. However, as we mentioned earlier, in the present series, we did not observe any smectic phase even up to trans-p-n-dodecyloxy- α -methylcinamic acid. Therefore, the smectic phase is more affected as a result of the introduction of the α -methyl group into a trans-p-n-alkoxycinamic acid.

2.3 p-Cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates: Preparation and mesomorphic behaviour

As mentioned earlier the present study concerns the preparation of materials having a high positive dielectric anisotropy. It is known that Ph-CN has a moment of 4.05 D.²² Therefore, it was decided to study the liquid crystalline properties of a homologous series of esters of the acids

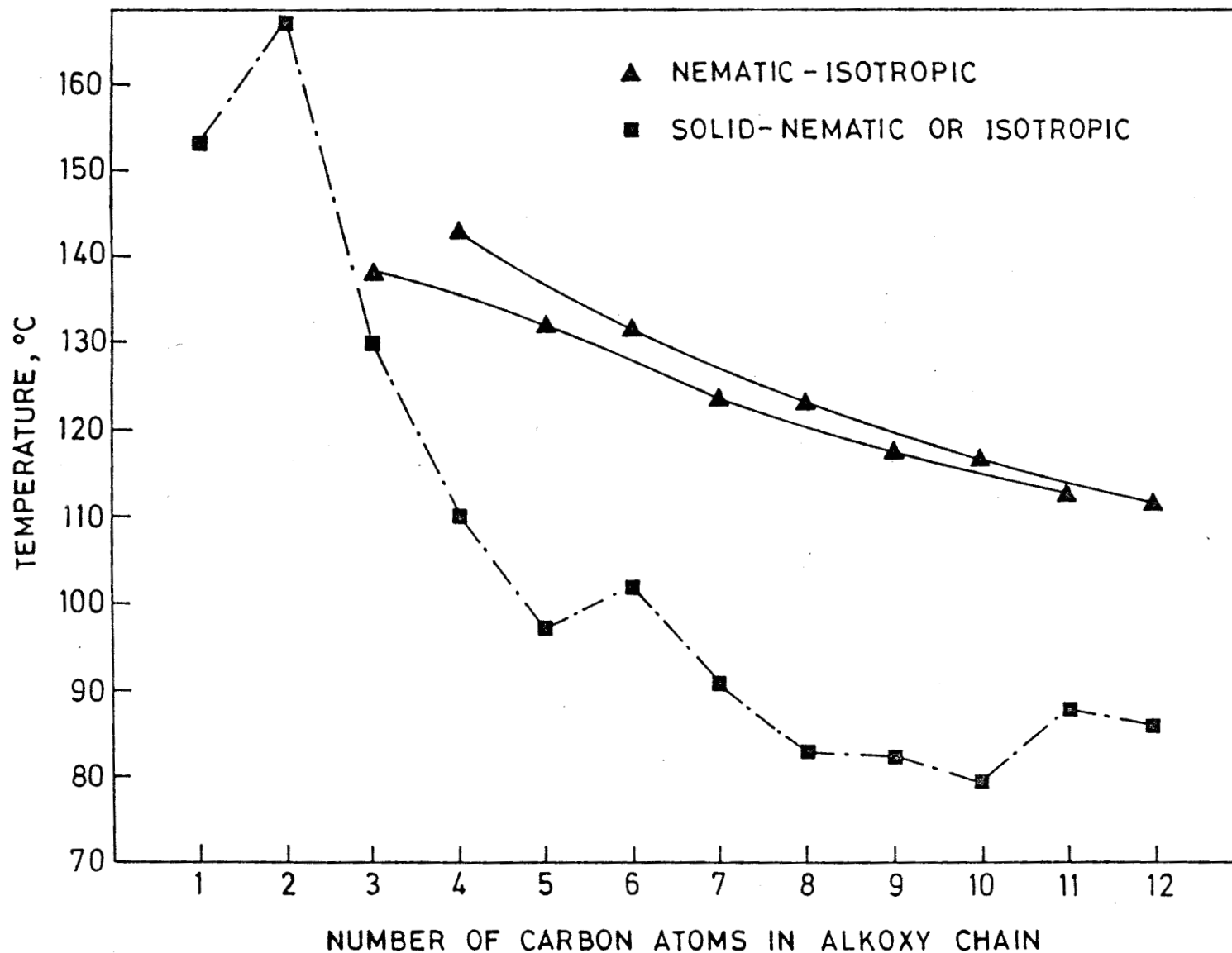


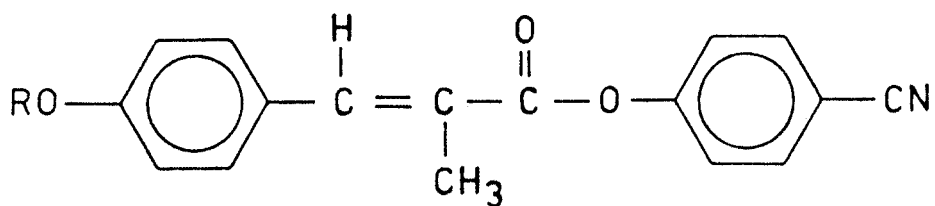
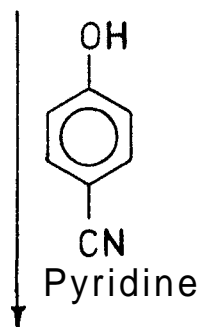
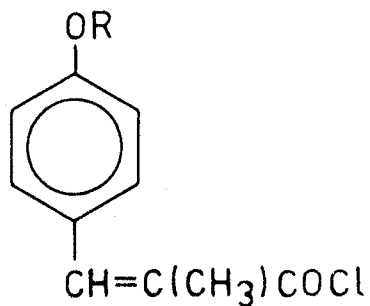
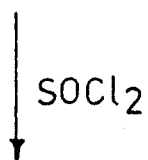
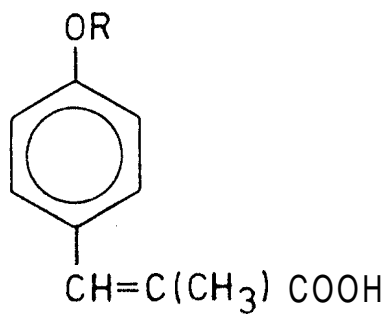
Figure 2.2: Plot of transition temperatures against number of carbon atoms in the alkoxy group for trans-p-n-alkoxy- α -methylcinnamic acids.

discussed in section 2.2, with p-hydroxybenzotrile. The p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates were prepared by treating the appropriate cinnamic acid chloride with p-hydroxybenzotrile in pyridine solution at room temperature (Chart II). The esters were obtained as colourless products.

The transition temperatures *for* this series of compounds are summarised in table 2.3. It is seen that the clearing temperatures for the entire series is below 80°. Five of the twelve homologues are monotropic nematic and the rest are enantiotropic mesomorphic. The smectic phase of compounds 10, 11 and 12 shows a simple fan-shaped texture as shown in plate 1 and is believed to be smectic A. A measurement of the elastic constants²³ for compound 10, close to the smectic-nematic transition, supports this view. Moreover, by analogy with many of the known materials of high positive dielectric anisotropy showing a smectic A phase,^{24,25,26} this can also be classified as smectic A. We reported²⁶ earlier that compound 10 showed another smectic phase with a schlieren texture. In fact, it has been recently found²⁷ that this is a 're-entrant nematic phase'. The occurrence of the re-entrant nematic phase has been discussed in greater detail in the next chapter.

The effect of the α -methyl group on the mesophase

CHART II



R = n-Alkyl

Table 2.3

Transition temperatures of p-cyanophenyl trans-p'-n-alkoxy-
 α -methylcinnamates

Compound number	R= <u>n</u> -alkyl	Temperature of transition to			
		Re-entrant nematic °C	Smectic °C	Nematic °C	Isotropic °C
1	CH ₃	-	-	(77.2)	112.5
2	C ₂ H ₅	-	-	79	90.3
3	C ₃ H ₇	-	-	(67.1)	70
4	C ₄ H ₉	-	-	68.3	74.2
5	C ₅ H ₁₁	-	-	(64)	90.5
6	C ₆ H ₁₃	-	-	(70.5)	83
7	C ₇ H ₁₅	-	-	(67.5)	71
8	C ₈ H ₁₇	-	-	58.5	71.9
9	C ₉ H ₁₉	-	-	63	70.9
10	C ₁₀ H ₂₁	32.5	(59)	62	74
11	C ₁₁ H ₂₃	-	(70.3)	70.3	73.7
12	C ₁₂ H ₂₅	-	61	-	76.1

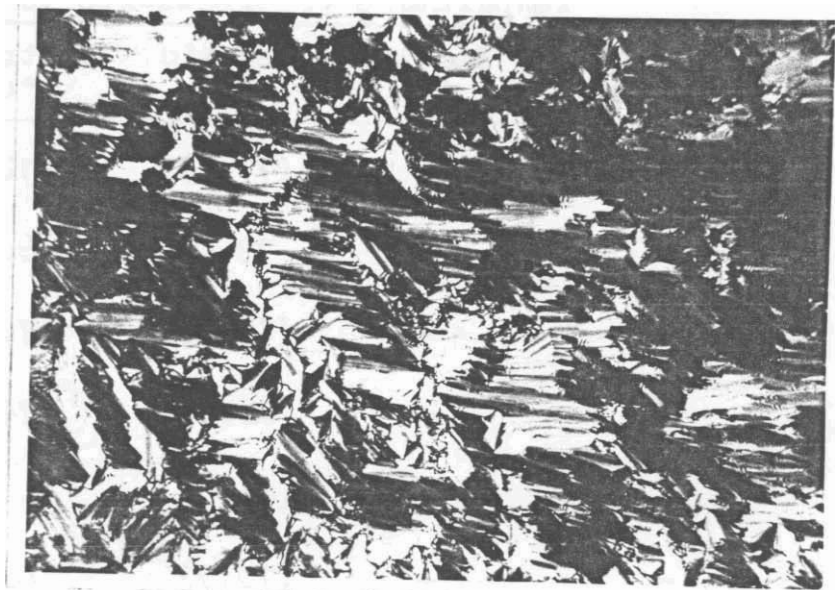


Plate 1

transition temperatures shows some interesting features. A comparison of the melting and clearing temperatures of the first eight homologues of p-cyanophenyl trans-p'-n-alkoxycinnamates prepared by Titov et al²⁸ with the present series shows that there is an average decrease of about 70° for T_{H-I} in the case of the substituted compounds. Comparing this result with that on the acid series discussed in section 2.2, we find that the α -methyl substituent has opposite effect, on the nematic range in the two series. However, the average decrease in the melting points is not marked and is only about 16°. Thus, the nematic range is considerably decreased in the substituted compounds clearly demonstrates that no definite prediction of the melting points can be made from the molecular structure. Titov et al²⁸ do not mention of any smectic phase up to the p-cyanophenyl trans-p'-n-octyloxycinnamate and the higher homologues of this series are not known. However, in the present series the smectic phase appears from p-cyanophenyl trans-p'-n-decyloxy- α -methylcinnamate. In compounds 10 and 11, the smectic phase is monotropic, whereas in compound 12 it is enantiotropic (table 2.3). Since the higher homologues of the parent series are not known it would be difficult to comment on the effect of the substituent on the smectic thermal stabilities. Unlike in the case of the acid series discussed in the previous section, the α -methyl group does

not come in the way of the formation of the smectic phase in the ester series.

The reduction in T_{N-I} may be explained as due to some significant structural effect. The ester molecule could take up either of the two possible conformations (I) or (II) shown in figure 2.3. In both these conformers the thickening effect arising due to steric effect between the α -methyl group and the ortho ring protons, mentioned earlier is present and would tend to lower the transition temperatures. In conformer (II) where the α -methyl group and the carbonyl group are on the same side, there is a broadening of the molecule. This broadening would also be expected to lower transition temperature. In conformer (I) the α -methyl and the carbonyl groups are on opposite sides. This conformation is sterically more favoured and free rotation around the =C-C- single bond is unlikely since this bond has some

$$\begin{array}{c} \text{=C-C-} \\ | \quad || \\ \text{CH}_3 \quad \text{O} \end{array}$$

double bond character due to resonance. However, it is likely that at least a fraction of the molecules have the conformation (II) so that there would also be some contribution of the broadening effect towards the lowering of the transition temperatures. The reduction of about 70° in T_{N-I} in the p-cyanophenyl trans-p'-n-alkoxy- α -methyl cinnamates can be attributed to these factors.

Figure 2.4 shows the plot of the transition temperatures

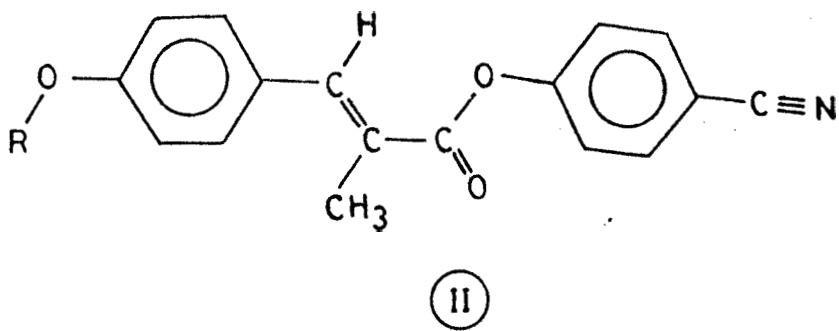
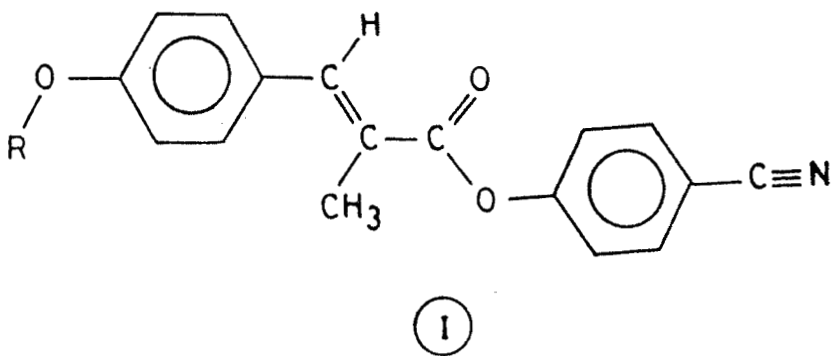


Figure 2.3

Molecular structure and two possible conformations of the rigid part of p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates.

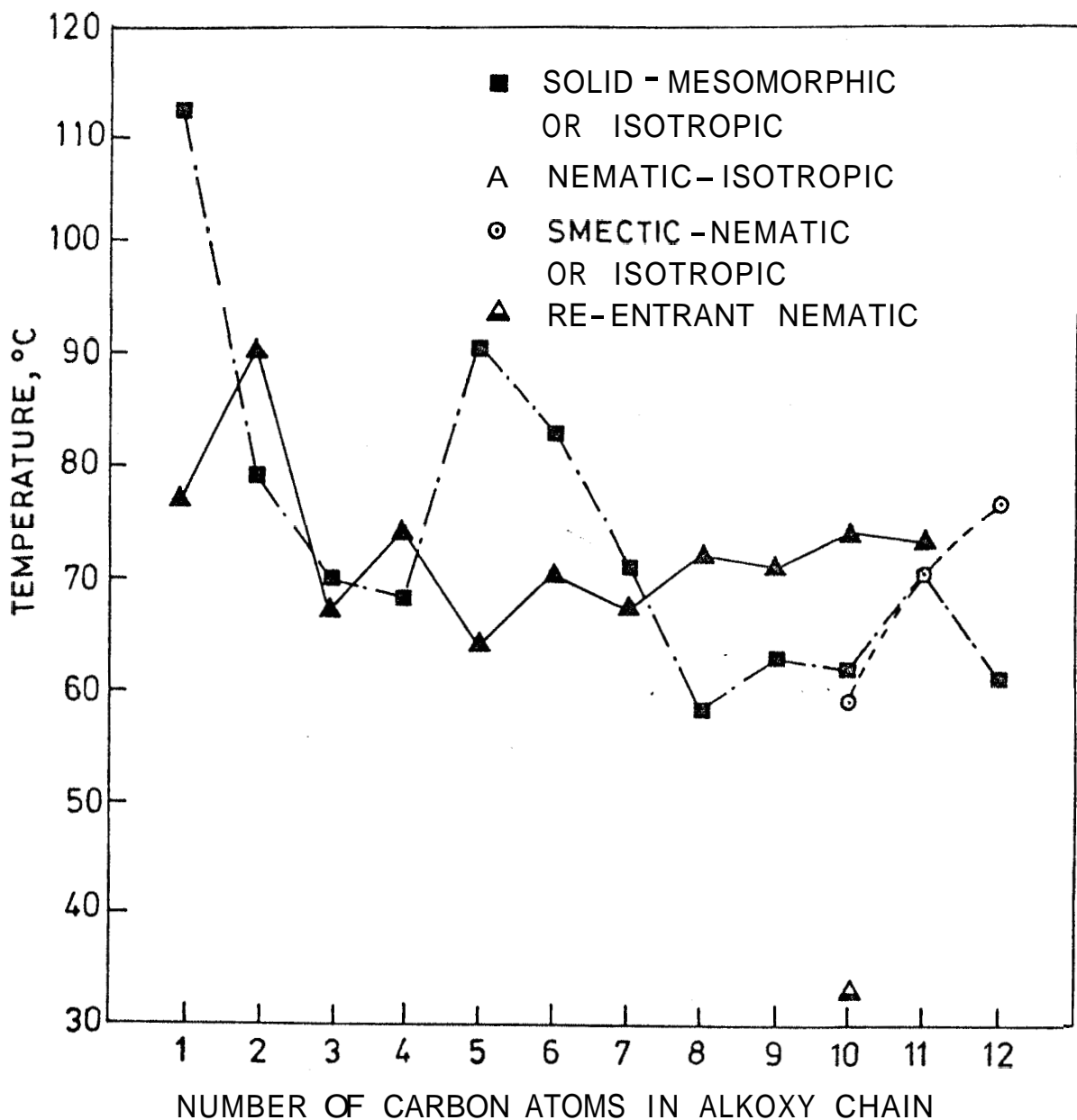


Figure 2.4

Plot of transition temperatures against number of carbon atoms in the alkoxy group for *p*-cyanophenyl trans-*p'*-*n*-alkoxy- α -methylcinnamates.

against the number of carbon atoms in the alkoxy chain for the p-cyanophenyl trans-p'-n-alkoxy- α -methyl cinnamates. This has some interesting features. Usually, T_{N-I} for a homologous series decreases on ascending the series. Deviations from this type of behaviour are known, wherein these transition points show an upward trend as the terminal carbon chain length is increased. Gray⁸ has reported a series of 2'-substituted N-(p-n-alkoxybenzylidene)-p'-aminobiphenyls, whose transition points show an upward trend. He has attributed this to a decrease in the ratio of lateral to terminal interactions because of the broadening of the molecules due to steric hindrance. Castellano *et al*²⁹ reported a series of N-(p-n-alkoxybenzylidene)-p'-aminoacetophenones, which also deviated from normal behaviour. They have suggested that this might be due to the strong terminal attractions originating from the acetyl group which would result, as in the above case a low ratio of lateral to terminal cohesions. However, it must be pointed out that there are several other series of compounds with similar strong permanent dipoles, which show a normal descending trend. Deitrich and Steiger³⁰ reported a series of N-(p-n-alkoxybenzylidene)-p'-butylanils which showed an upward trend for the transition points. They concluded, "that ascending mesomorphic transition temperature functions are likely to occur in homologous series of overall low

intermolecular cohesiveness". Marcelja,³¹ based on theoretical calculations has concluded that in a homologous series with higher transition temperatures, these temperatures decrease with increasing end-chain length. He has attributed this to rather strong anisotropic interaction between the rigid structures of the molecule and that the addition of end chains decrease the average anisotropic interaction. However, in a series with low transition temperatures the addition of molecular and chains increase the average anisotropic interaction between the molecules. Some homologous series of compounds are known^{12,32,33} which show an upward trend.

Figure 2.4 shows a mixed trend for T_{N-I} points, with an initial decrease up to the pentyloxy derivative, and a gradual increase from thereon. This may be due to the various possible conformational changes in the alkyl chain. Young and co-workers³⁴ who have obtained thermodynamic data on a homologous series of aldonitrone, have come to the conclusion that the conformation of the chain in the nematic phase is not fixed in a series. A possible explanation of the observed trend in figure 2.4 is as follows. The lateral substituent (α -methyl group) evidently increases the lateral dimensions (breadth and thickening) of the molecule. It would appear that under these circumstances, the gauche conformation of the end chain for the first few members of

the homologous series does not enhance the maximum lateral dimensions of the molecule and therefore there is an increased probability of its occurrence. This conformation decreases the anisotropy of polarisability and hence decreases T_{N-I} . Interestingly Pink³⁵ has put forward a similar model based on theoretical calculations. This might happen up to the pentyloxy derivative which has a minimum in the curve. The relative probability of the existence of the 'all trans' or 'zig-zag' conformation would appear to increase at this stage and the increasing residual lateral attractions, which assist in the maintenance of the nematic order come into play. The result is that T_{N-I} curve rises as the terminal alkyl chain grows longer.

Another feature in this series is that the curve joining the smectic-nematic or isotropic points does not merge with the curve joining the nematic-isotropic points. This has again been explained by Gray⁸ as due to a less efficient packing of the molecules which in turn is due to a steric effect as discussed earlier.

2.4 Thermodynamic properties

The enthalpies and entropies of transition for the homologous series of p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates have been summarised in table 2.4. It was difficult to get the DSC trace of p-cyanophenyl trans-p'-methoxy- α -

Table 2.4

Transition enthalpies and entropies of a homologous series of p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates

Compound number	R=n-Alkyl group	Transition	Transition heat ΔH , kcal/mole	Transition entropy ΔS , kcal/mole/°K
1	Methyl	K \rightarrow I	6.38	16.56
		N \rightarrow I	-	-
2	Ethyl	K \rightarrow N	4.11	11.68
		N \rightarrow I	0.84	0.23
3	Propyl	K \rightarrow I	4.5	13.12
		N \rightarrow I	0.57	0.16
4	Butyl	K \rightarrow N	6.5	19
		N \rightarrow I	0.10	0.29
5	Pentyl	K \rightarrow I	9.1	25
		N \rightarrow I	0.82	0.24
6	Hexyl	K \rightarrow I	6.92	19.45
		N \rightarrow I	0.10	0.3
7	Heptyl	K \rightarrow I	6.64	19.31
		N \rightarrow I	0.11	0.34
8	Octyl	K \rightarrow N	7.94	23.92
		N \rightarrow I	0.12	0.37
9	Nonyl	K \rightarrow N	11.62	34.59
		N \rightarrow I	0.15	0.44
10	Decyl	K \rightarrow N	11.12	33.19
		S \rightarrow N	0.003	0.01
		N \rightarrow I	0.18	0.52

...

Table 2.4continued

Compound number	R-n-Alkyl group	Transition	Transition heat ΔH , kcal/mole	Transition entropy ΔS , kcal/mole/°K
11	Undecyl	K \rightarrow N	10.38	30.22
		S \rightarrow N	0.02	0.05
		N \rightarrow I	0.16	0.46
12	Dodecyl	K \rightarrow S	11.43	34.23
		S \rightarrow I	0.61	1.75

methylcinnamate as the mesophase solidified immediately after its formation. Hence the ΔH and ΔS values for this compound have not been given. All the transitions were found to be first order although the smectic-nematic transition was accompanied by rather small enthalpies. However, it is known³⁶ that many smectic A-nematic transitions are weakly first order or may even be second order. This is due to the fact that a slight longitudinal displacement of the molecules from the smectic A layers is sufficient to give rise to the nematic mesophase. The transition enthalpies for compounds exhibiting a monotropic phase was obtained by reheating the supercooled mesophases. The enthalpies for the nematic-isotropic transition are of the order of 0.1 to 0.5 kcal/mole.

Figure 2.5 shows the relationship between the entropy change and the alkoxy chain length for the series *p*-cyanophenyl trans-*p'*-*n*-alkoxy- α -methylcinnamates. There is an alternation for N-I transition up to C₆ after which there is a continuous increase up to C₁₁. However, there is a small decrease for C₁₂. The smectic-nematic transition which occurs in only two of the compounds in this series has very low entropy change. The entropy change accompanying a crystal-mesophase or isotropic transition along the homologous series is random. However, the general tendency is that there is an increase in entropy as the series is ascended.

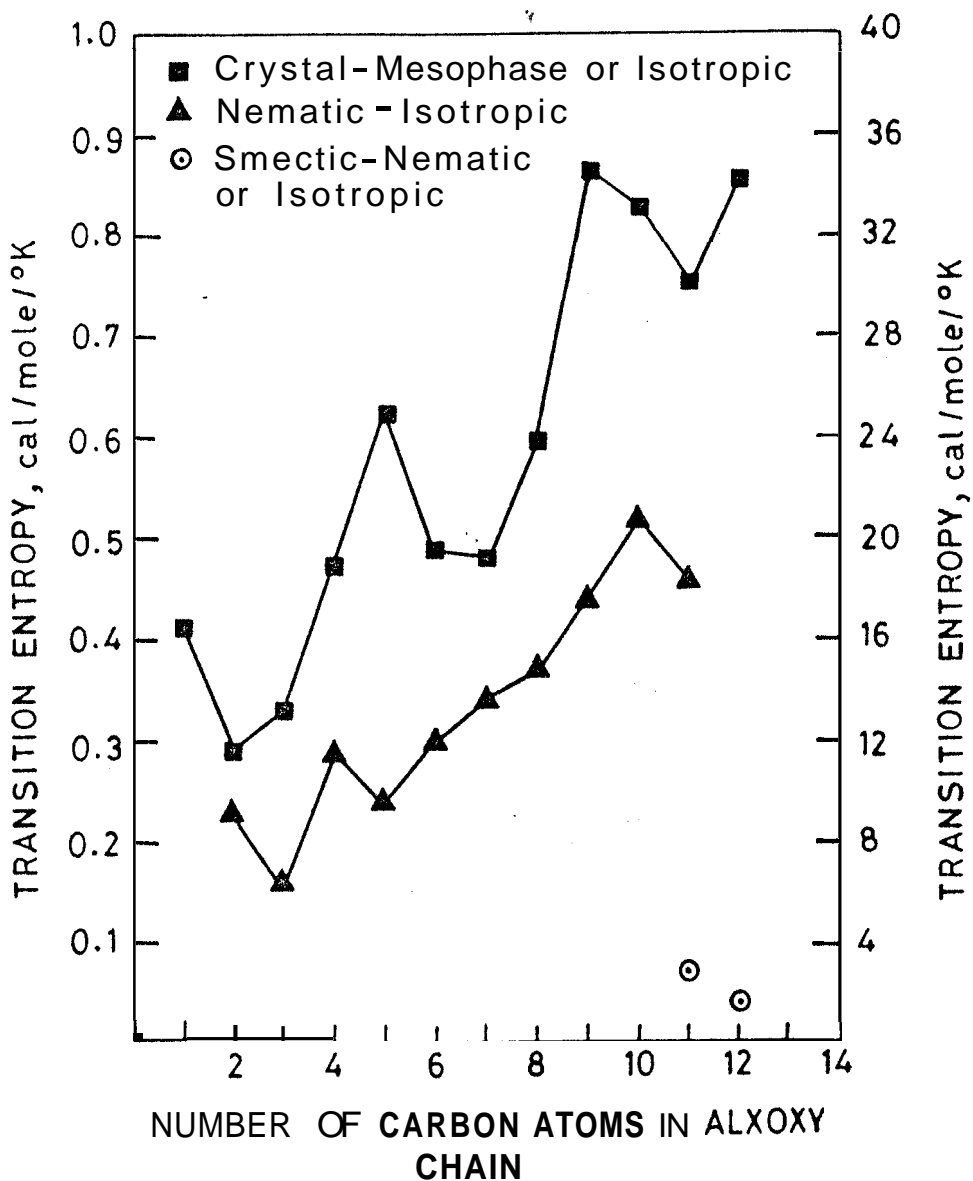


Figure 2.5

Transition entropies for p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates.

2.5 Dielectric properties of p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates

As mentioned in section 2.1, the interest in these compounds is that they have strong positive dielectric anisotropy. The principal dielectric constants and dielectric anisotropy for this series measured by Ratna³⁷ are given in table 2.5.

Table 2.5

Principal dielectric constants and dielectric anisotropy of p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates at $(T_{N-I} - 1)^{\circ}C$

Compound number (see table 2.3)	$\epsilon_{ }$	ϵ_{\perp}	$\Delta\epsilon$
2	22.22	10.27	11.95
4	19.80	10.00	9.80
8	16.88	9.11	7.77
9	14.79	8.04	6.75
10	14.16	7.95	6.21
11	13.97	8.05	5.92

As can be seen from this table, for all the compounds $\epsilon_{||}$ is about twice ϵ_{\perp} . The large dielectric anisotropy is mainly due to the presence of the terminal $-CN$ group.

capillary tubes using a microscope Franz Kustner Nacht KG, Dresden, Model HKK 70/3171 provided with a heating stage. The transitions were also studied by differential scanning calorimetry using a Perkin-Elmer Model DSC-2. The enthalpy and entropy values were calculated by measuring the areas under the peaks on the recording chart paper, knowing the weight of the sample and the area given by a known weight of a standard sample for which the enthalpy of melting is known accurately. Pure Indium was used as the standard. The mesophase textures were observed, by sandwiching samples between a glass slide and cover slip, under a polarising microscope.

p-Ethoxybenzaldehyde

A solution of sodium ethoxide was prepared by adding sodium (2.3 g, 0.1 mol) in small pieces to absolute ethyl alcohol (100 ml) taken in a 250 ml round bottom flask fitted with a reflux condenser and a drying tube. p-Hydroxybenzaldehyde (12.2 g, 0.1 mol) was added to this solution and the mixture was stirred and refluxed for fifteen minutes. Ethyl iodide (17.1 g, 0.11 mol) was added through the condenser and the stirring and refluxing continued for a further period of four hours and cooled. Ethyl alcohol was removed by distillation under reduced pressure and the residue was dissolved in ether (150 ml). This was washed with 10% sodium hydroxide solution (2x50 ml) and water (2x50 ml) and dried (Na_2SO_4). Removal of solvent afforded a liquid which was distilled under reduced pressure to give p-ethoxybenzaldehyde (14.0 g, 93%), b.p. $90^\circ/1$ mm (reported yield 65.75%, b.p. $106^\circ/3$ mm).

The physical data of the cognate preparations of

other p-n-alkoxybenzaldehydes are given in table 2.6.

Anisaldehyde was obtained commercially and distilled before use.

trans-p-Ethoxy- α -methylcinnamic acid

This was prepared following the procedure of Johnson.²⁰ Thus, a mixture of p-ethoxybenzaldehyde (9.0 g, 0.06 mol), propionic anhydride (9.75 g, 0.075 mol) and potassium propionate (6.72 g, 0.06 mol) was heated in oil bath at 130°C for thirty hours. The warm reaction mixture was poured on to a stirred mixture of concentrated hydrochloric acid (10 ml) and ice-cold water (50 ml). The pale brown semi-solid hardened after about thirty minutes. It was filtered off, washed with water, dried and recrystallised from 95% ethyl alcohol to constant m.p. (10.2 g, 82%, m.p. 167°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 1674, 1604, 1503, 1180 and 1040 cm^{-1} ; λ_{max} 282 nm (ϵ , 4.25); 6 (DMSO- d_6) 1.34 (s, 3H, $-\text{CH}_3$) 2.04 (d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$) 4.05 (q, 2H, $-\text{OCH}_2-$) 6.96-7.6 (m, 5H, arH and vinyl H) 12.43 (s, 1H, $-\text{COOH}$)

[Found: C, 69.96; H, 7.08% $\text{C}_{12}\text{H}_{14}\text{O}_2$ requires
C, 69.902; H, 6.796%].

Table 2.6Physical constants of *p*-*n*-alkoxybenzaldehydes, $\text{R}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$

R =	Observed		Reported		
	B.P. °C/mm	Yield %	B.P. °C/mm	Yield %	Reference
C_3H_7	100-102/2	82	141-143/20	48	38
C_4H_9	110/2	82.5	155-157/20	64	38
C_5H_{11}	150-153/5	90.5	163-166/10	54	38
C_6H_{13}	142-145/2	73.5	177-180/10	71	38
C_7H_{15}	155-157/8	73.5	143-146/5	58	38
C_8H_{17}	180-184/2	83.5	141-144/0.1	40	38
C_9H_{19}	185-189/2	75	163-166/05	42	38
$\text{C}_{10}\text{H}_{21}$	135-140/0.1	71.5	185/4	65-75	2
$\text{C}_{11}\text{H}_{23}$	185/1	64.5	-	-	-
$\text{C}_{12}\text{H}_{25}$	160-163/1	74.5	194/8	65-75	2

The physical data of the cognate preparations of other trans-p-n-alkoxy- α -methylcinnamic acids are given below.

trans-p-Methoxy- α -methylcinnamic acid

Yield 84%, m.p. 153°C; $\nu_{\text{max}}^{\text{nujol}}$ 1670, 1601, 1518, 1430, 1325, 1134, 1032 and 832 cm^{-1} ; λ_{max} 281 nm (ϵ 4.39); δ (DMSO- d_6) 2.04 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.79 (s, 3H, $-\text{OCH}_3$) 6.9-7.6 (m, 5H, arH and vinyl H) 12.38 (s, 1H, $-\text{COOH}$)
[Found: C, 68.68; H, 6.43% $\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C, 68.75; H, 6.25%].

trans-p-propoxy- α -methylcinnamic acid

Yield 79%, m.p. 130.1°C; $\nu_{\text{max}}^{\text{nujol}}$ 1676, 1603, 1517, 1185, 1134, 1020 and 818 cm^{-1} ; λ_{max} 283 nm (ϵ 4.26); δ (DMSO- d_6) 0.98 (t, 3H, $-\text{CH}_3$) 1.67-1.8 (m, 2H, $-\text{CH}_2-$) 2.03 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.96 (t, 2H, $-\text{OCH}_2-$) 6.97-7.56 (m, 5H, arH and vinyl H) 12.46 (s, 1H, $-\text{COOH}$)
[Found: C, 70.84; H, 7.45% $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.90; H, 7.27%].

trans-p-Butoxy- α -methylcinnamic acid

Yield 86%, m.p. 110°C; $\nu_{\text{max}}^{\text{nujol}}$ 1680, 1603, 1518, 1133, 1142 and 820 cm^{-1} ; λ_{max} 281 nm (ϵ 4.27); δ (DMSO- d_6) 0.93 (t, 3H, $-\text{CH}_3$) 1.3-1.8 (m, 4H, methylenes) 2.03 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.99 (t, 2H, $-\text{OCH}_2-$) 6.9-7.55 (m, 5H, arH and

vinyl H) 12.38 (s, 1H, -COOH)

[Found: C, 72.16; H, 8.09% $C_{14}H_{18}O_3$ requires
C, 71.79; H, 7.69%].

trans-p-Pentyloxy- α -methylcinnamic acid

Yield 80%, m.p. 97°C; ν $\frac{\text{nujol}}{\text{max}}$ 1670, 1600, 1510, 1180,
1020 and 837 cm^{-1} ; λ_{max} 281 nm (ϵ 4.25); δ (DMSO- d_6) 0.89
(t, 3H, -CH₃) 1.30-1.74 (m, 6H, methylenes) 2.03 [d, 3H,
-CH=C(CH₃)] 3.98 (t, 2H, -OCH₂) 6.96-7.55 (m, 5H, arH and
vinyl H) 12.41 (s, 1H, -COOH)

[Found: C, 73.09; H, 7.76% $C_{15}H_{20}O_3$ requires
C, 72.58; H, 8.06%].

trans-p-Hexyloxy- α -methylcinnamic acid

Yield 72%, m.p. 102°C; ν $\frac{\text{nujol}}{\text{max}}$ 1680, 1604, 1520, 1425,
1270, 1186, 1026 and 838 cm^{-1} ; λ_{max} 281 nm (ϵ 4.26);
 δ (DMSO- d_6) 0.87 (t, 3H, -CH₃) 1.2-1.75 (m, 8H, methylenes)
2.03 [d, 3H, -CH=C(CH₃)] 3.98 (t, 2H, -OCH₂) 6.9-7.6 (m, 5H,
arH and vinyl H) 12.39 (s, 1H, -COOH)

[Found: C, 73.24; H, 8.30% $C_{16}H_{22}O_3$ requires
C, 73.28; H, 8.39%].

trans-p-Heptyloxy- α -methylcinnamic acid

Yield 79%, m.p. 93°C; ν $\frac{\text{nujol}}{\text{max}}$ 1672, 1601, 1518, 1320,

1181 and 833 cm^{-1} ; λ_{max} 281 nm (ϵ 4.27); δ (DMSO- d_6)
0.86 (t, 3H, $-\text{CH}_3$) 1.2-1.8 (m, 10 H, methylenes) 2.03
[a, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.99 (t, 2H, $-\text{OCH}_2$) 6.9-7.6 (m, 5H,
arH and vinyl H) 12.37 (s, 1H, $-\text{COOH}$)

[Found: C, 74.01; H, 8.95% $\text{C}_{17}\text{H}_{24}\text{O}_3$ requires
C, 73.91; H, 8.69%].

trans-p-Octyloxy- α -methylcinnamic acid

Yield 83%, m.p. 83°C; $\gamma_{\text{max}}^{\text{nujol}}$ 1676, 1601, 1518, 1180,
1021 and 838 cm^{-1} ; λ_{max} 281 nm (ϵ 4.29); δ (DMSO- d_6) 0.86
(t, 3H, $-\text{CH}_3$) 1.2-1.71 (m, 12H, methylenes) 2.03 [d, 3H,
 $-\text{CH}=\text{C}(\text{CH}_3)$] 3.98 (t, 2H, $-\text{OCH}_2$) 6.90-7.75 (m, 5H, arH and
vinyl H) 12.36 (s, 1H, $-\text{COOH}$)

[Found: C, 74.38; H, 8.90% $\text{C}_{18}\text{H}_{26}\text{O}_3$ requires
C, 74.48; H, 8.96%].

trans-p-Nonyloxy- α -methylcinnamic acid

Yield 71%, m.p. 82.5°C; $\gamma_{\text{max}}^{\text{nujol}}$ 1680, 1602, 1512,
1182, 1014 and 839 cm^{-1} ; λ_{max} 282 nm (ϵ 4.25); δ (DMSO- d_6)
0.85 (t, 3H, $-\text{CH}_3$) 1.2-2.0 (m, 14H, methylenes) 2.03 [d, 3H,
 $-\text{CH}=\text{C}(\text{CH}_3)$] 12.38 (s, 1H, $-\text{COOH}$)

[Found: C, 75.25; H, 9.34% $\text{C}_{19}\text{H}_{28}\text{O}_3$ requires
C, 75.00; H, 9.21%].

trans-p-n-Decyloxy- α -methylcinnamic acid

Yield 82%, m.p. 79.5°C; γ nujol λ_{\max} 1680, 1604, 1512, 1300, 1184 and 838 cm^{-1} ; λ_{\max} 281 nm (ϵ 4.27); δ (DMSO- d_6) 0.85 (t, 3H, $-\text{CH}_3$) 1.24 - 1.73 (m, 16H, methylenes) 2.03 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.98 (t, 2H, $-\text{OCH}_2$) 6.96-7.55 (a, 5H, arH and vinyl H) 12.35 (s, 1H, $-\text{COOH}$)

[Found: C, 75.88; H, 9.60% $\text{C}_{20}\text{H}_{30}\text{O}_3$ requires C, 75.47; H, 9.43%].

trans-p-n-Undecyloxy- α -methylcinnamic acid

Yield 71%, m.p. 88.2°C; γ nujol λ_{\max} 1682, 1601, 1512, 1250, 1182, 1024 and 836 cm^{-1} ; λ_{\max} 282 nm (ϵ 4.27); δ (DMSO- d_6) 0.85 (t, 3H, $-\text{CH}_3$) 1.24-1.73 (m, 18H, methylenes) 2.03 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.98 (t, 2H, $-\text{OCH}_2$) 6.95-7.55 (m, 5H, arH and vinyl H) 12.38 (s, 1H, $-\text{COOH}$)

[Found: C, 75.91; H, 9.79% $\text{C}_{21}\text{H}_{32}\text{O}_3$ requires C, 75.90; H, 9.63%].

trans-p-n-Dodecyloxy- α -methylcinnamic acid

Yield 79%, m.p. 86°C; γ nujol λ_{\max} 1680, 1601, 1512, 1300, 1250, 1182 and 838 cm^{-1} ; λ_{\max} 281 nm (ϵ 4.27); δ (DMSO- d_6) 0.85 t 3H, $-\text{CH}_3$) 1.14-1.73 (m, 20H, methylenes) 2.03 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.98 (t, 2H, $-\text{OCH}_2$) 6.95-7.55 (m, 5H, arH and vinyl H) 12.35 (s, 1H, $-\text{COOH}$)

[Found: C, 76.28; H, 9.91% $\text{C}_{22}\text{H}_{34}\text{O}_3$ requires C, 76.30; H, 9.82%].

p-Cyanophenyl trans-p'-ethoxy- α -methylcinnamate

trans-p-Ethoxy- α -methylcinnamic acid (4.12 g, 0.02 mol) was refluxed with redistilled thionyl chloride (29.52 g, 0.25 mol) for three hours, at the end of which excess thionyl chloride was removed by distillation under reduced pressure. p-Hydroxybenzonnitrile (2.38 g, 0.02 mol) in anhydrous pyridine (30 ml) was added all at once to the crude acid chloride, the mixture being stirred magnetically for three hours at room temperature and left overnight. The reaction mixture was poured on to a stirred mixture of concentrated hydrochloric acid (60 ml) and crushed ice (150 g), when a precipitate was obtained. It was filtered, washed with water, 10% sodium hydroxide solution, water and dried. The crude material was chromatographed on silica gel and eluted with benzene. Removal of solvent from the eluate afforded a white product which was crystallised from benzene-petroleum ether (40-60°C) to constant melting point (5.6 g, 91%) m.p. 80°C; ν_{max} 2240, 1725, 1602, 1518, 1303, 1264 and 918 cm^{-1} ; λ_{max} 232 nm (ϵ 4.38), 312 nm (ϵ 4.47); δ (CDCl_3) 1.44 (t, 3H, $-\text{CH}_3$) 2.25 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 4.15 (q, 2H, $-\text{OCH}_2$) 6.8-7.9 (m, 5H, arH and vinyl H)

[Found: C, 74.58; H, 5.45; N, 4.46% $\text{C}_{19}\text{H}_{17}\text{O}_3\text{N}$ requires C, 74.27; H, 5.53; N, 4.56%].

The physical data of the cognate preparations of other p-cyanophenyl trans-p'-n-alkoxy- α -methylcinnamates are given below.

p-Cyanophenyl trans-p'-methoxy- α -methylcinnamate

Yield 85%, m.p. 112.5°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2240, 1710, 1608, 1518, 1328, 1220, 1085 and 832 cm^{-1} ; λ_{max} 232 nm (ϵ 4.32) 311 nm (ϵ 4.47); δ (CDCl_3) 2.23 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.83 (s, 3H, $-\text{OCH}_3$) 6.8-7.93 (m, 9H, arH, and vinyl H)

[Found: C, 73.65; H, 5.32; N, 4.64% $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$ requires C, 73.72; H, 5.12; N, 4.77%].

p-Cyanophenyl trans-p'-propoxy- α -methylcinnamate

Yield 82%, m.p. 70°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2240, 1725, 1603, 1572, 1380, 1170, 974 and 839 cm^{-1} ; λ_{max} 232 nm (ϵ 4.32) 312 nm (ϵ 4.48); δ (CDCl_3) 1.06 (t, 3H, $-\text{CH}_3$) 1.85 (q, 2H, $-\text{CH}_2-$) 2.25 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.98 (t, 2H, $-\text{OCH}_2-$) 6.73-8.0 (m, 9H, arH and vinyl H)

[Found: C, 74.55; H, 5.84; N, 4.28% $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}$ requires C, 74.76; H, 5.92; N, 4.36%].

p-Cyanophenyl trans-p'-n-butoxy- α -methylcinnamate

Yield 83%, m.p. 74.2°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2240, 1725, 1603, 1390, 1212, 1183, 890 and 810 cm^{-1} ; λ_{max} 232 nm (ϵ 4.31) 311 nm (ϵ 4.46); δ (CDCl_3) 1.0 (t, 3H, $-\text{CH}_3$) 1.16-2.1 (m, 6H, methylenes) 2.26 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 4.01 (t, 2H, $-\text{OCH}_2-$)

6.86-8.0 (m, 9H, arH and vinyl H)

[Found: C, 75.18; H, 5.98; N, 4.05% $C_{21}H_{21}O_3$ requires
C, 75.23; H, 6.27; N, 4.18%].

p-Cyanophenyl trans-p'-n-pentyloxy- α -methylcinnamate

Yield 79%, m.p. 90.5°C, γ nujol_{max} 2240, 1725, 1605,
1516, 1470, 952, 843 and 745 cm^{-1} ; λ_{max} 232 nm (ϵ 4.33)
312 nm (ϵ 4.47); δ (CDCl₃) 0.98 (t, 3H, -CH₃) 1.16-2.1
(m, 6H, methylenes) 2.23 [d, 3H, -CH=C(CH₃)] 4.01 (t, 2H,
-OCH₂-) 6.76-8.06 (m, 9H, arH and vinyl H)

[Found: C, 75.41; H, 6.53; N, 3.92% $C_{22}H_{23}O_3$ requires
C, 75.65; H, 6.59; N, 4.01%].

p-Cyanophenyl trans-p'-n-hexyloxy- α -methylcinnamate

Yield 81%, m.p. 83°C, γ nujol_{max} 2240, 1725, 1603, 1516,
1380, 1225, 1143, 1075 and 882 cm^{-1} ; λ_{max} 232 nm (ϵ 4.32)
312 nm (ϵ 4.46); δ (CDCl₃) 0.93 (t, 3H, -CH₃) 1.13-2.1
(m, 8H, methylenes) 2.26 [d, 3H, -CH=C(CH₃)] 4.03 (t, 2H,
-OCH₂-) 6.9-8.1 (m, 9H, arH and vinyl H)

[Found: C, 76.39; H, 7.46; N, 3.70% $C_{23}H_{25}O_3$ requires
C, 76.03; H, 6.83; N, 3.85%].

p-Cyanophenyl trans-p'-n-heptyloxy- α -methylcinnamate

Yield 73%, m.p. 71°C, γ nujol_{max} 2240, 1723, 1602, 1516,
1470, 1310, 1084, 893 and 745 cm^{-1} ; λ_{max} 232 nm (ϵ 4.32)
312 nm (ϵ 4.46); δ (CDCl₃) 0.9 (t, 3H, -CH₃) 1.1-2.1 (m, 10H,

methylene) 2.25 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 4.05 (t, 2H, $-\text{OCH}_2-$)
6.9-8.06 (m, 9H, arH and vinyl H)

[Found: C, 76.54; H, 7.38; N, 3.78% $\text{C}_{24}\text{H}_{27}\text{O}_3\text{N}$ requires
C, 76.39; H, 7.16; N, 3.71%].

p-Cyanophenyl trans-p'-n-octyloxy- α -methylcinnamate

Yield 76%, m.p. 58.5°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2240, 1722, 1601,
1518, 1329, 890 and 845 cm^{-1} ; λ_{max} 231 nm (ϵ 4.33) 312 nm
(ϵ 4.45); δ (CDCl_3) 0.87 (t, 3H, $-\text{CH}_3$) 1.11-2.13 (m, 12H,
methylene) 2.23 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 3.99 (t, 2H, $-\text{OCH}_2-$)
6.77-7.93 (m, 9H, arH and vinyl H)

[Found: C, 77.08; H, 7.66; N, 3.48% $\text{C}_{25}\text{H}_{29}\text{O}_3\text{N}$ requires
C, 76.72; H, 7.41; N, 3.58%].

p-Cyanophenyl trans-p'-n-nonyloxy- α -methylcinnamate

Yield 87%, m.p. 63°C; γ $\begin{matrix} \text{nujol} \\ \text{max} \end{matrix}$ 2240, 1725, 1603,
1512, 1310, 1074, 1015, 913 and 832 cm^{-1} ; λ_{max} 231 nm
(ϵ 4.32) 312 nm (ϵ 4.47); δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$)
1.15-2.13 (a. 14H, methylene) 2.23 [d, 3H, $-\text{CH}=\text{C}(\text{CH}_3)$] 4.0
(t, 2H, $-\text{OCH}_2-$) 6.82-7.95 (m, 9H, arH and vinyl H)

[Found: C, 77.40; H, 8.06; N, 3.79% $\text{C}_{26}\text{H}_{31}\text{O}_3\text{N}$ requires
C, 77.03; H, 7.65; N, 3.45%].

p-Cyanophenyl trans-p'-n-decyloxy- α -methylcinnamate

Yield 81%, m.p. 62°C; ν nujol max 2240, 1722, 1601, 1565, 1380, 1310, 1120, 1018, 835 and 718 cm^{-1} ; λ max 232 nm (ϵ 4.33) 312 nm (ϵ 4.48); δ (CDCl_3) 0.88 (t, 3H, $-\text{CH}_3$) 1.16-2.04 (m, 16H, methylenes) 2.19 [d, 3H, $-\text{CH}=\text{O}(\text{CH}_3)$] 3.94 (t, 2H, $-\text{OCH}_2-$) 6.74-7.82 (m, 9H, arH and vinyl H)
[Found: C, 77.14; H, 7.96; N, 3.25% $\text{C}_{27}\text{H}_{33}\text{O}_3\text{N}$ requires C, 77.32; H, 7.87; N, 3.34%].

p-Cyanophenyl trans-p'-n-undecyloxy- α -methylcinnamate

Yield 74%, m.p. 70.3°C; ν nujol max 2240, 1725, 1603, 1512, 1380, 1308, 1205, 1075, 914 and 834 cm^{-1} ; λ max 231 nm (ϵ 4.32) 312 nm (ϵ 4.48); δ (CDCl_3) 0.87 (t, 3H, $-\text{CH}_3$) 1.11-1.97 (m, 18H, methylenes) 2.18 [d, 3H, $-\text{CH}=\text{O}(\text{CH}_3)$] 3.94 (t, 2H, $-\text{OCH}_2-$) 6.71-7.8 (m, 9H, arH and vinyl H)
[Found: C, 77.68; H, 8.24; N, 3.15% $\text{C}_{28}\text{H}_{35}\text{O}_3\text{N}$ requires C, 77.59; H, 8.08; N, 3.23%].

p-Cyanophenyl trans-p'-n-dodecyloxy- α -methylcinnamate

Yield 80%, m.p. 61°C; ν nujol max 2240, 1725, 1603, 1578, 1380, 1180, 1025, 887 and 820 cm^{-1} ; λ max 232 nm [ϵ 4.31] 311 nm (ϵ 4.47); δ (CDCl_3) 0.86 (t, 3H, $-\text{CH}_3$) 4.0 (t, 2H, $-\text{OCH}_2-$) 6.78-8.05 (m, 9H, arH and vinyl H)
[Found: C, 77.95; H, 8.25; N, 3.08% $\text{C}_{29}\text{H}_{37}\text{O}_3\text{N}$ requires C, 77.85; H, 8.27; N, 3.13%].

REFERENCES

1. O.M. Bennett and B. Jones, *J. Chem. Soc.* 420 (1939).
2. G.W.Gray and B. Jones, *J.Chem.Soc.* 1467 (1954).
3. G.W.Gray, B. Jones and Y. Marson, *J.Chem.Soc.*1417 (1956).
4. M. Lesclercq, J. Billard and J. Jacques, *Mol. Cryst. Liq. Cryst.* 10, 429 (1970).
5. G.W.Gray and K.J.Harrison, *Mol. Cryst. Liq. Cryst.* 13, 37 (1971).
6. A. Hochapfel, D. Berchet, R. Peron and J. Petit, *Mol. Cryst. Liq. Cryst.* 13, 165 (1971).
7. J.S.Dave and R.A.Vora, *Mol.Cryst.Liq.Cryst.* 14, 319 (1971).
8. G.W.Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, Inc., London and New York (1962) ch.9.
9. G.W.Gray, *Mol. Cryst. Liq. Cryst.* 7, 127 (1969).
10. W.R.Young, I. Haller and D.C.Green, *J.ORG.Chem.* 27, 3707 (1972).
11. R.J.Oak, *Mol.Cryst.Liq.Cryst.* 19, 111 (1972).
12. Y.Y.Hsu and D. Dolphin, *Liquid Crystals and Ordered Fluids*, Vol. 2, Ed. J.F.Johnson and R.S.Porter, Plenum Press, New York (1974), p. 461.
13. Z.G.Gardlund, R.J.Curtis and G.W.Smith, *Chem. Comm.* 202 (1973).

14. W.R.Young, A.Aviram and R.J.Cox,, J.Amer.Chem.Soc. 94, 3976 (1972).
15. M.M.Leclercq, J.Billard and J.Jacques, Mol.Cryst.Liq. Cryst. 8, 367 (1969).
16. J. van der Veen and A.H.Grobbe, Mol.Cryst.Liq.Cryst. 15, 239 (1971).
17. F.B.Jones and J.J.Ratto, Chem.Comm. 21, 841 (1973).
18. F.B.Jones and J.J.Ratto, Liquid Crystals and Ordered Fluids, Vol. 2, Ed. J.F.Johnson and R.S.Porter, Plenum Press, New York (1974), p.723.
19. F.B.Jones and J.J.Ratto, J.Physique, 36, C1-413 (1975).
20. J.R.Johnson, Organic Reactions, Vol.1, Ed. R.Adams, W.E.Bachmann, L.F.Fieser, J.R.Johnson and H.R.Snyder, John Wiley and Sons, New York (1942), p.210.
- 21.(a) G.W.Gray, J.B.Hartley, A.Ibbotson and B. Jones, J.Chem.Soc. 4359 (1955).
(b) G.W.Gray, J.Chem.Soc. 552 (1958).
(c) G.W.Gray and K.J.Harrison, Liquid Crystals, Vol. 3, Ed. G.H.Brown, and M.M.Lebes, Gordon and Breach Science Publishers (1972), p. 557.
22. V. Minkin, O. Osipov and Y.Zhdanov, Dipole Moments in Organic Chemistry, Plenum Press, New York (1970).
23. P.P.Karat, Ph.D. Thesis, Mysore University (1977).
24. G.W. Gray and A. Mosley, Mol. Cryst. Liq. Cryst. 37, 213 (1976).

25. G.W.Gray and D.G.McDonnell, *Mol.Cryst.Liq.Cryst.* 37, 189 (1976).
26. J.C.Dubois and A. Zann, *J.Physique*, ^{36,} 03-35 (1976).
27. N.V.Madhusudana, B.K.Sadashiva and K.P.L.Moodithaya, *Curr. Sci.* 48, 613 (1979).
28. V.V. Titov, E.I. Kovshov, A.I.Pavluchenko, V.T.Lazareva and M.P.Grebenkin, *J.Physique*, 36, 01-387 (1975).
29. J.A.Castellano, J.E.Goldmacher, L.A.Barton and J.S.Kane, *J. Org. Chem.* 33, 3501 (1968).
30. H.J.Deitrich and E.L.Steiger, *Mol. Cryst.Liq. Cryst.*, 16, 263 (1972).
31. S. Marcelja, *J.Chem.Phys.* 60, 3599 (1974).
32. M.E.Neubert, L.T.Carlino, R.D'sidocky and D.L.Fishel, *Liquid Crystals and Ordered Fluids, Vol.2*, Ed.J.F.Johnson and R.S.Porter, Plenum Press, New York (1973), p.293.
33. G.W.Gray, K.J.Harrison, J.A.Nash, J.Constant, D.S.Hulme, J. Kirton and E.P.Raynes, *ibid.* 617 (1973).
34. W.R.Young, I.Haller and A.Aviram, *IBM J.Res.Develop.* 15, 41 (1971).
35. D.A.Pink, *J.Chem.Phys.* 63(6), 2533 (1975).
36. B.Cabane and W.G.Clark, *Sol.State Comm.* 13, 129 (1973).
37. B.R.Ratna, Ph.D. Thesis, Mysore University (1978).
38. T.R.Criswell, B.H.Klandermann and D.C.Batesky, *Mol.Cryst. Liq. Cryst.* 22, 211 (1973).