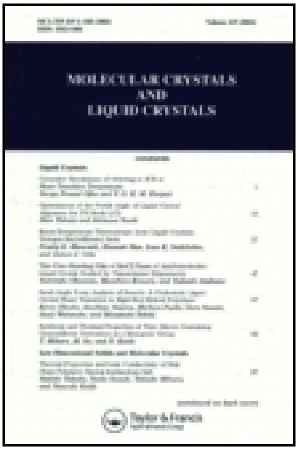

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Mesomorphic Properties of Some α-Methyl Cinnamic Acids and their Esters

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Mesomorphic Properties of Some α-Methyl Cinnamic Acids and their Esters

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Two homologous series of liquid crystalline substances have been synthesized and their mesomorphic properties studied. These are (i) *trans-p-n*-alkoxy-α-methyl cinnamic acids and (ii) *trans-p-n*-alkoxy-α-methyl-*p*′-cyanophenyl cinnamates. The esters are colourless and fairly low melting materials of high positive dielectric anisotropy. The effect of the α-methyl group on the mesomorphic thermal stability of both the homologous series is discussed and compared with other materials of similar structure. The nematic–isotropic transition temperatures in ascending series of the esters show an initial decrease and then a gradual increase, which is not a commonly observed phenomenon for homologous series of liquid crystalline substances.

INTRODUCTION

During the last few years much attention and effort have been devoted to the synthesis of new liquid crystalline compounds of low melting points and suitable nematic ranges. Recent work on cinnamic acid esters by Jones and Ratto[1] has shown that these are low melting compounds with wide nematic ranges, a large positive dielectric anisotropy and rather high nematic isotropic transition temperatures. It is known[2–5] that lateral substituents, either at the *ortho* position on a phenyl ring or the α-position of a central linkage will reduce both the solid–mesomorphic and mesomorphic–isotropic transition temperatures markedly when compared with the unsubstituted parent compounds. The extent of reduction of the temperature depends on the size of the lateral substituents and the shape of the substituted molecules. With this in view and also as a part of a programme of study of the structure and properties of liquid crystals, two new homologous series of twelve compounds each have been synthesised and their mesomorphic properties characterised. These are the *trans-p-n*-alkoxy-α-methyl cinnamic acids and their esters with 4-hydroxy benzonitrile. The esters have a large dielectric anisotropy, because of the fact that Ph—CN has a group moment of 4.05 D.[6] The effect of the α-methyl group on the mesomorphic transition temperatures of these two homologous series shows some interesting features.

EXPERIMENTAL

The transition temperatures were determined in open capillary tubes using a microscope (Franz Kustner Nacht KG, Dresden, Model HMK 70/3171) provided with a heating stage. The mesophase textures were observed in thin films, by sandwiching samples between a glass slide and cover slip, under a polarizing microscope.

p-n-Alkoxy benzaldehydes were prepared as described by Weygand and Gabler,[7] but in higher yields than were reported by these authors. *trans-p-n*-Alkoxy-α-methyl cinnamic acids were synthesised according to the procedure of Johnson.[8] All new acids and esters had satisfactory spectral properties and elemental analyses. Infrared spectra were recorded on a Leitz double beam prism spectrograph,[9] ultraviolet spectra were obtained on a UNICAM SP 700 A ultraviolet and visible spectrophotometer and NMR spectra were taken either on a Varian HA-100 or T-60 spectrometer. The purity of the materials was also checked by thin layer chromatography. A typical procedure for the preparation of an acid and its ester is given below.

trans-p-Ethoxy-α-methyl cinnamic acid A mixture of *p*-ethoxybenzaldehyde (9 g, 0.06 mol), propionic anhydride (9.75 g, 0.075 mol) and potassium propionate (6.72 g, 0.06 mol) was heated in an oil bath at 130°C for 30 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 30 minutes. It was filtered off, washed with water, dried and recrystallised from 95% ethyl alcohol to a constant melting point. Yield 81%, m.p. 167°C, Ir (nujol) 1685 cm^{-1} (carboxyl c = 0); UV max (95% C_2H_5OH) 282 nm (ε 4.25); NMR ($CDCl_3$) δ 1.02 (t-3, C*H*$_3$ of C_2H_5O), 1.68 (d-3 CH_2), 3.67 (q-2, C*H*$_2$ of C_2H_5O), 6.6–7.6 (m-5 aromatic and ethylenic).

Anal: Calcd. for $C_{12}H_{14}O_2$: C, 69.902; H, 6.796
Found: C, 69.95; H, 7.08

trans-p-Ethoxy-α-methyl-p′-cyanophenyl cinnamate *trans-p*-Ethoxy-α-methyl cinnamic acid (4.12 g, 0.02 mol) was refluxed for three hours with redistilled thionyl chloride (29.52 g, 0.25 mol), at the end of which excess thionyl chloride was removed by distillation under reduced pressure.

4-Hydroxybenzonitrile (2.38 g, 0.02 mol) in anhydrous pyridine (30 ml) was added in one lot to the crude acid chloride, the mixture being stirred magnetically for three hours at room temperature and left overnight. This reaction mixture was poured onto a stirred mixture of concentrated hydrochloric acid (60 ml) and crushed ice (150 g), when the ester precipitated. It was filtered, washed with water, 10% sodium hydroxide solution, water and dried. Yield 97%. The crude ester was chromatographed on silica gel (BDH, India, 60–120 mesh) and eluted with benzene. Removal of solvent from the eluate afforded a white material, which was recrystallised from light petroleum (b.p. 40–60°C) and benzene several times until the melting point was constant. m.p. 80°C. Ir (nujol) 2240 cm^{-1} ($C \equiv N$) 1725 cm^{-1} (ester $C = O$); UV max (95% C_2H_5OH) 232 nm (ε 4.38) 312 nm (ε 4.47); NMR (CCl_4) δ 1.44 (t-3, CH_3 of C_2H_5O) 2.25 (d-3, CH_3) 4.15 (q-2, CH_2 of C_2H_5O) 6.8–7.9 (m-9, aromatic and ethylenic).

Anal: Calcd. for $C_{19}H_{17}NO_3$: C, 74.27; H, 5.53; N, 4.56
Found: C, 74.58; H, 5.45; N, 4.46.

RESULTS AND DISCUSSION

The transition temperatures of *trans-p-n*-alkoxy-α-methyl cinnamic acids are summarised in Table I. Figure 1 shows a plot of the transition temperatures against the number of carbon atoms in the alkoxy chain. This is the general trend that has been observed by a number of researchers in the

TABLE I

Melting and clearing temperatures for *trans-p-n*-alkoxy-α-methyl cinnamic acids. $ROC_6H_4CH{:}C(CH_3)COOH$

Compound number	R[a]	K → N or I °C	N → I °C	ΔT°C nematic range
13	$—CH_3$	157.5-159	—	—
14	$—C_2H_5$	167	—	—
15	$—C_3H_7$	132	138.8	6.8
16	$—C_4H_9$	110	143	33
17	$—C_5H_{11}$	99	132.1	33.1
18	$—C_6H_{13}$	104.8	132	27.2
19	$—C_7H_{15}$	93.5	123.6	30.1
20	$—C_8H_{17}$	86.2	123	36.8
21	$—C_9H_{19}$	85.5	117.5	32.0
22	$—C_{10}H_{21}$	80.5	116.5	36.0
23	$—C_{11}H_{23}$	89.8	112.5	22.7
24	$—C_{12}H_{25}$	89	112.1	23.1

[a] All alkyl groups are normal

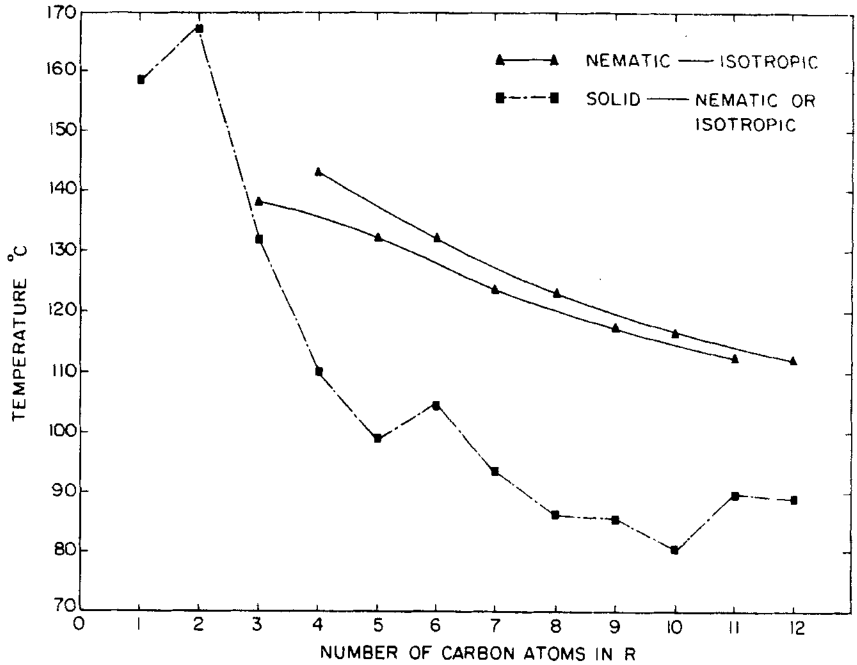
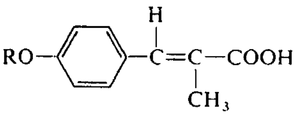
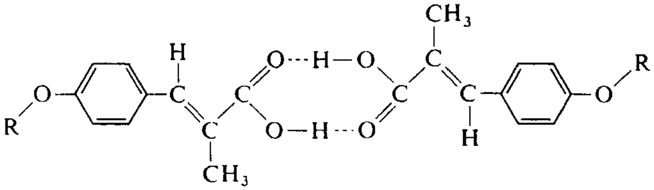


FIGURE 1



Plot of transition temperatures against the number of C atoms in the alkoxy chain for the *trans-p-n*-alkoxy-α-methyl cinnamic acids.

field, in that, the nematic-isotropic transition temperature decreases in the ascending series. It is seen that for these compounds the transition points lie on two smooth falling curves. The curve for the even homologues lies above the curve for the odd homologues. A similar trend has been observed for the unsubstituted parent homologues synthesized by Gray *et al.*[10] In that series all the homologues are enantiotropic mesomorphic and the smectic phase commences at *trans-p-n*-nonyloxy cinnamic acid. In the present series compounds 13 and 14 (refer Table I) are non-mesomorphic or in other words the isotropic melts do not sufficiently supercool to exhibit the monotropic mesophases, as in the case of *p*-methoxy- and *p*-ethoxy benzoic acids.[11] The smectic phase could not be detected even in compound 24. The dimeric form of the *trans-p-n*-alkoxy-α-methyl cinnamic acid (I) with a *trans* configuration is shown below.



I

The α-methyl group of the central linkage has a pronounced effect on the mesophase transition temperatures when compared with the unsubstituted parent compounds. Apart from a decrease in the melting points, the smectic mesophase is more affected than the nematic mesophase. This is in accordance with Gray's[12] work on various mesomorphic homologous series of compounds, which show a similar behaviour. A comparison of the melting points and clearing points of *trans-p-n*-alkoxy cinnamic acid series and the present series reveals that there is an average decrease of about 44°C in the melting points and 51°C in the clearing points. It is interesting to note that the thermal range of the mesophase has increased, as a result of the introduction of the α-methyl group when compared with the unsubstituted parent acids. The reduction in transition temperature has been attributed to a thickening effect[19] caused by a steric interaction of the α-methyl group with the *ortho* ring protons. This will interfere with the close packing of the molecules and increase the molecular separation and decrease the strength of the intermolecular attractions.

The transition temperatures for the *trans-p-n*-alkoxy-α-methyl-*p′*-cyanophenyl cinnamates are summarised in Table II. It is seen that the clearing temperatures of the entire series is below 80°C. Five of the twelve homologues are monotropic nematic and the rest are enantiotropic mesomorphic. Compound 12 is purely smectic and compound 9 has the lowest melting point of 56°C in the series, is purely nematic, and has a thermal range of 14.3°C. The smectic phases of compound 10, 11 and 12 show a simple fan-shaped texture and are believed to be smectic A. A measurement of the elastic constants[13] for compound 10, close to the smectic–nematic transition, supports this view. This compound exhibits another smectic phase which has a schlieren texture just before it solidifies. This has a very short phase length and consequently could not be identified. A comparison of the melting and clearing temperatures of the first eight homologues of *trans-p-n*-alkoxy-*p′*-cyanophenyl cinnamates,[14] with the present series shows that there is an average decrease of about 70°C for the nematic–isotropic transition temperatures. However, the average decrease in the melting points is not marked and is only about 16°C. This once again[15]

TABLE II

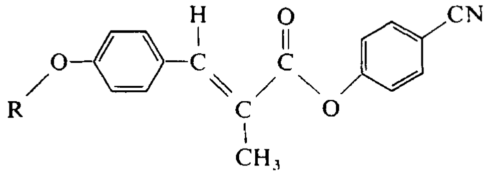
Transition temperatures for *trans-p-n*-alkoxy-α-methyl *p*′-cyanophenyl cinnamates. $RO \cdot C_6H_4 \cdot CH{:}C(CH_3)COO \cdot C_6H_4 \cdot CN$

Compound number	R[a]	Temperature of transition to Smectic °C	Nematic °C	Isotropic °C
1	CH_3	—	(77.2)	110.5–111.5
2	C_2H_5	—	80	90.6
3	C_3H_7	—	(66.6)	70.5–71
4	C_4H_9	—	63	73.8
5	C_5H_{11}	—	(63.2)	91–91.5
6	C_6H_{13}	—	(70.8)	83.5–84
7	C_7H_{15}	—	(67.5)	71–71.5
8	C_8H_{17}	—	58	72
9	C_9H_{19}	—	56	70.3
10[b]	$C_{10}H_{21}$	(57.1)	62.8	73.5
11	$C_{11}H_{23}$	(70)	70	73.2
12	$C_{12}H_{25}$	65	—	76.2

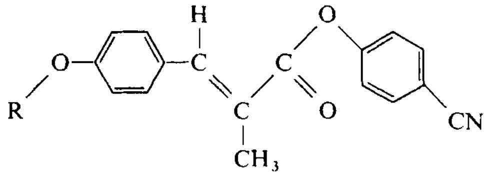
[a] All alkyl groups are normal. Transition temperatures in parentheses indicate monotropic transitions.

[b] This compound shows two smectic phases.

demonstrates that a prediction of the melting points cannot be made from the molecular structure. The reduction in the transition temperatures may be explained on the basis of some significant structural effect. The ester molecule[a] could take up either of the two possible conformations II or III.



II



III

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[a] The author thanks the referee for these comments.

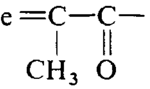
In both of these conformers, the thickening effect mentioned earlier is present and would tend to lower the transition temperatures. The molecule in conformer III is also broadened by the presence of both the α-methyl and the carbonyl groups on the same side which would also be expected to lower the transition temperatures. This does not occur in conformer II where the α-methyl and the carbonyl groups are on opposite sides. Conformer II is sterically more favored and free rotation around the  $=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-$ is unlikely since the single bond probably has some double bond character due to resonance. However, it is likely that at least some of conformer III is present so that there would also be some contribution of the broadening effect towards the lowering of the transition temperatures. As a consequence of these factors the reduction of about 70°C in the nematic–isotropic transition temperatures in the α-methyl cinnamic acid esters may be understood.

Figure 2 shows the plot of the transition temperatures against the number of carbon atoms in the alkoxy chain for the *trans-p-n*-alkoxy-α-methyl-*p*′-cyanophenyl cinnamates. This has some interesting features. Usually, the nematic–isotropic transition temperatures of homologous series decrease in ascending series. Deviations from this type of behavior are known,[16] wherein these temperatures show an upward trend as the carbon chain length is increased. Figure 2 shows a different behavior for these transition points, with an initial decrease up to compound 5, and a gradual increase from then on. A similar trend was observed for the *p*-isobutyl phenyl-*p*′-alkoxy benzoates,[17] but no suitable explanation has been given. It is believed that this may be due to the various possible conformational changes in the alkyl chain. Young and co-workers[18] who have obtained thermodynamic data on a homologous series of aldonitrones, have come to the conclusion that the conformation of the chain is not fixed in the series. A possible explanation of the observed trend is described below. 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 polarizability anisotropy and hence decreases the nematic–isotropic transition temperature. It is interesting to note that recently Pink[20] has put forward a similar model. This might happen up to compound 5 which has a minimum in the curve. The relative probability of the all-*trans* or 'zig-zag' conformation would appear to increase at this stage and all the interactions postulated by Gray[19] come into play so that there is an increase in the nematic–isotropic transition

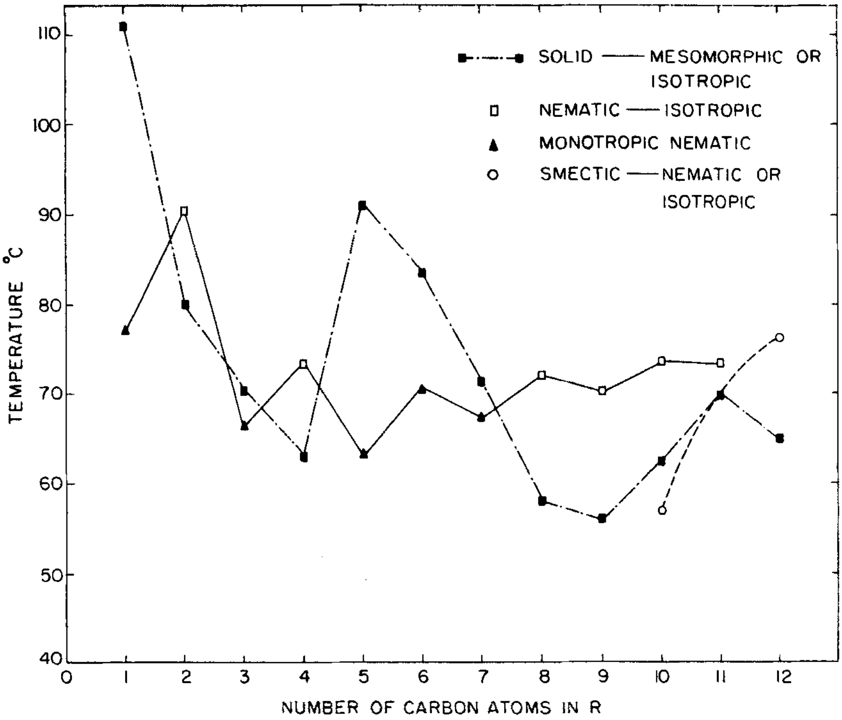
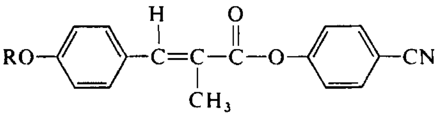


FIGURE 2



Plot of transition temperatures against the number of C atoms in the alkoxy chain for the *trans-p-n*-alkoxy-α-methyl *p'*-cyanophenyl cinnamates.

temperatures of the higher homologues. Another interesting feature of this homologous series is seen in the curve joining the smectic–nematic or isotropic transition temperatures. Normally, the smectic–nematic or isotropic curve merges with the falling nematic–isotropic curve at the decyloxy or dodecyloxy derivative. In the present case, the smectic–nematic or isotropic curve rises initially as expected but does not merge with the rising portion of nematic–isotropic curve.

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