New mesogenic homologous series of **a**-methylcinnamates

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Abstract. Compounds of a new smectogenic homologous series of **a**-methyl-cinnamates were prepared by condensing different 4-*n*-alkoxybenzoyl chloride with methoxyethyl *trans*-4-hydroxy-**a**-methylcinnamate. In this series, the first six members are non-mesogenic. *n*-Heptyloxy derivative exhibits monotropic smectic A phase whereas rest of the members exhibit enantiotropic smectic A mesophase. The compounds are characterized by combination of elemental analysis and spectroscopic techniques. Enthalpies of few homologues are measured by DSC techniques. Fluorescent properties are also observed. The thermal stabilities of the present series are compared with those of other structurally related mesogenic homologous series.

Keywords. Smectic A; ambient temperature; **a**-methylcinnamates.

1. Introduction

The advent of applications of liquid crystals in optical display devices led to an upsurge in the synthesis of room temperature nematic liquid crystals. Subsequently, it was established that smectic A as well as chiral smectic C phases have applications in advanced liquid crystal displays. This led to design of molecules which exhibit low melting smectic A and smectic C phases. Esters normally show smectic phases. Cinnamate esters have been well known for over 30 years and extensive literature exists[1–13]. Vora and Rajput[14] have reported binary mixtures of cinnamate esters exhibiting wide ranges of smectic and nematic mesophases. Recently, Sadashiva *et al*[15] reported two mesogenic homologous series of cinnamate esters exhibiting ferroelectric and antiferroelectric phases. Aromatic esters with a broken alkoxy chain in the ester linkage have been less studied. In our previous study[16], we reported that compounds containing a methoxyethyl and ethoxyethyl ester linkage exhibited SmA phase at ambient temperatures. In order to learn more about the effect of such ester linkage on mesomorphism, methoxyethyl *trans*-4(4′-*n*-alkoxybenzoyloxy)-*a*-methylcinnamates of the following structural formula (**1**) were synthesized and their mesogenic properties investigated.

$$RO-\text{⬡}-COO-\text{⬡}-CH=\underset{\underset{CH_3}{|}}{C}-COOCH_2CH_2OCH_3 \qquad \textbf{1}$$

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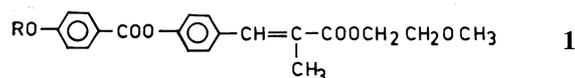
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2. Experimental

2.1 *Characterization*

The chemical structures of intermediates and final compounds were confirmed by using a combination of elemental analysis (Coleman carbon–hydrogen analyser), infrared spectroscopy (Shimadzu IR-408) and ^{1}H NMR spectroscopy (Perkin–Elmer R-32). Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. DSC was investigated on a Mettler TA-4000 system and fluorescent spectra was recorded on a Shimadzu Rf 540 spectrophotofluorometer.

2.2 *Synthesis*

4-Hydroxybenzaldehyde (BDH), propionic anhydride, sodium propionate, ethoxy ethanol, thionyl chloride (Sisco Chem), 4-hydroxybenzoic acid, *n*-alkyl halide (BDH) were used as received. All solvents were dried and distilled prior to use. The compounds of the new series (**1**) were prepared following the pathway shown in scheme 1.

$$R = -C_nH_{2n+1}, \; n = 4 \text{ to } 8, 10, 12, 14, 16$$
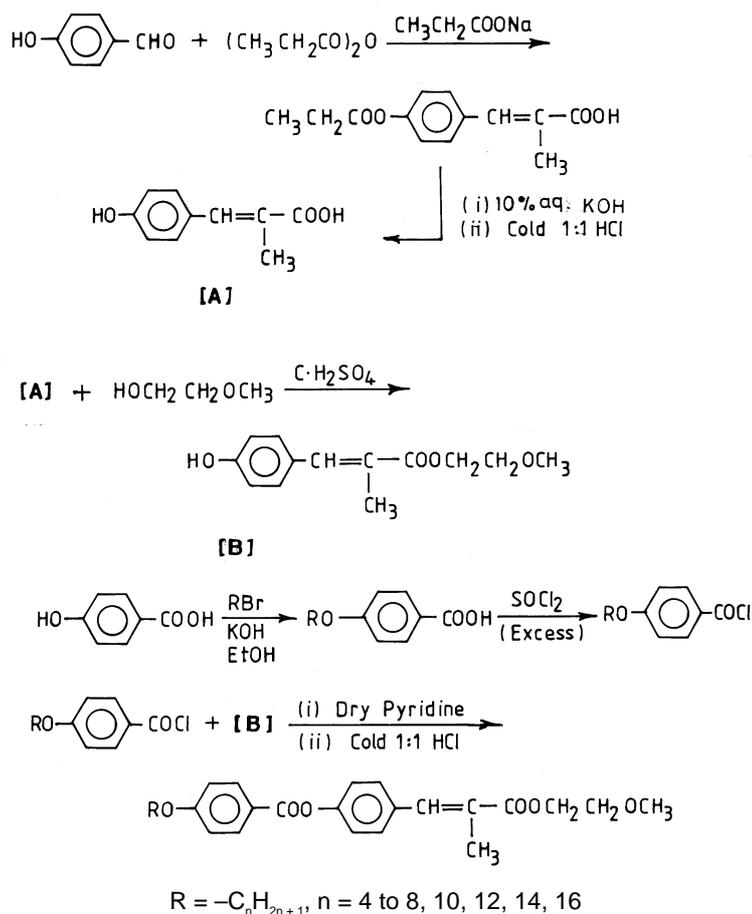
Scheme 1. Synthetic route to series **1**.

2.2a *trans-4-Hydroxy-**a**-methylcinnamic acid (A):* This compound was synthesized by the method reported by Perkin [17].

2.2b *Methoxyethyl trans-4-hydroxy-**a**-methylcinnamate (B):* This compound was prepared by the conventional method of esterification of *trans*-4-hydroxy-**a**-methyl cinnamic acid (A) with methoxyethanol using concentrated H_2SO_4 [18]. The ester was crystallized several times from aqueous methanol. Elemental analysis: Found, C 66·40, H 6·45%, $C_{13}H_{16}O_4$ requires C 66·10, H 6·78%. The IR (KBr) spectrum of the compound showed a broad peak of intermolecularly hydrogen bonded phenolic-OH between 3500 and 3100 cm^{-1}. The COO-stretching vibrations were seen at 1705 cm^{-1}. Other signals observed were at 1620 (–CH=C(CH$_3$)–), 1600, 1520, 1450, 1385, 1320, 1285, 1260, 1190, 1100, 1035, 990, 850, 760 cm^{-1}.

2.2c *4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides:* These were synthesized by the modified method of Dave and Vora [19].

2.2d *General procedure for synthesis of compounds (**1**):* Methoxyethyl *trans*-4-hydroxy-*a*-methylcinnamates (0·01 mole) was dissolved in dry pyridine (10 ml) and a cold solution of an appropriate 4-*n*-alkoxybenzoyl chloride (0·01 mole) in dry pyridine (10 ml) was added slowly to it with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 dilute hydrochloric acid. The product obtained was extracted with ether. The etheral extract was washed successively with water (2×30 ml), saturated solution of sodium bicarbonate (2×50 ml), 10% NaOH solution (2×50 ml) and water (2×30 ml). It was then dried (Na_2SO_4). The residue obtained on removal of solvent was chromatographed on silica gel using petroleum ether (60–80°C)-ethylacetate mixture (95:5) as eluent. Removal of solvent from the eluate afforded a solid material which was crystallized repeatedly from methanol. The purities of all these compounds were checked by thin layer chromatography (Merk Kiesel gel 60 F254 pre-coated plates). Melting points and transition temperatures are recorded in table 1. The elemental analyses of all the compounds were found to be satisfactory (table 2). IR (KBr, cm^{-1}) spectra: 2900, 1725 (–COO–), 1635 (–HC=C(CH$_3$)–), 1600, 1450, 1270, 1215, 1160, 1020, 840, 745.

Table 1. Transition temperatures (°C) for compounds (**1**).

| Compound no. | $R = -C_nH_{2n+1}$ | Transition temperatures (°C) | |
	n	SmA	**1**
1	4	–	73·0
2	5	–	41·0
3	6	–	38·0
4	7	(33·0)[a]	38·0
5	8	38·0	43·0
6	10	33·0	54·0
7	12	40·0	61·0
8	14	51·0	64·0
9	16	59·0	66·0

[a]Values in parentheses indicate monotropy

Table 2. Elemental analysis of data for compounds **1**.

Compound no. (table 1)	Molecular formula	Required (%)		Found (%)	
		C	H	C	H
1	$C_{24}H_{28}O_6$	69·90	6·80	69·63	7·08
2	$C_{25}H_{30}O_6$	70·42	7·04	70·05	7·14
3	$C_{26}H_{32}O_6$	70·91	7·27	70·48	7·08
4	$C_{27}H_{34}O_6$	71·37	7·49	71·14	7·43
5	$C_{28}H_{36}O_6$	71·79	7·69	71·37	7·26
6	$C_{30}H_{40}O_6$	72·58	8·07	73·00	8·31
7	$C_{32}H_{44}O_6$	73·28	8·40	73·41	7·96
8	$C_{43}H_{48}O_6$	73·91	8·69	73·48	8·85
9	$C_{36}H_{52}O_6$	74·48	8·96	74·96	8·56

Table 3. DSC data.

Compound no. (table 1)	Heating time (°C/min)	Transition	ΔH (J/g)	ΔS (J/gK)
8	10	Cr-SmA	39·37	0·1215
		SmA-**1**	1·93	0·0057
9	10	Cr-SmA	34·82	0·1048
		SmR-**1**	1·66	0·0049

^{1}H NMR (*n*-dodecyloxy derivative, 90 MHz, $CDCl_3$, standard TMS) *d* 0·9 (*t*, 3H, –C–CH₃), 1·1–1·7 (*brs*, 23H, $10 \times$ –CH₂– and –C=C– (CH₃)), 3·35 (*s*, 3H, –OCH₃), 3·65 (*t*, 2H, –COO–C–CH₂–), 4·0 (*t*, 2H, –PhOCH₂–), 4·3 (*t*, 2H, –COO–CH₂), 6·85 (*d*, *J* = 9 Hz, 2H at C-3′ and C-5′), 7·15 (*d*, *J* = 9 Hz, 2H at C-3 and C-5), 7·35 (*d*, *J* = 9 Hz, 2H at C-2 and C-6), 7·6 (*s*, 1H at –Ph–CH=C–), 8·0 (*d*, *J* = 9 Hz, 2H at C-2′ and C-6′), Enthalpies of *n*-tetradecyloxy and *n*-hexadecyloxy derivatives were measured by differential scanning calorimetry. Data are recorded in table 3.

3. Results and discussion

Lower members are non-mesogenic; the *n*-heptyloxy derivative exhibits monotropic smectic phase whereas rest of the members exhibit enantiotropic smectic phase. All the smectogens exhibit focal conic texture in polarizing microscope indicating that the smectic mesophase is of the SmA type. The type of smectic phase was further confirmed by miscibility study using 4-nitro-4′-*n*-decyloxy benzoate as standard material. An equimolar mixture of standard material and *n*-tetradecyloxy derivative of **1** was made by mixing them thoroughly in their isotropic states. (Transition temperatures (°C) of mixture: Cr 43·0 S_A 70·0 **1**). It is clear from this miscibility study that the smectic mesophase of *n*-tetradecyloxy derivative exhibited continuous miscibility with the smectic A mesophase of standard material. This indicated that smectogens of series (**1**) exhibited smectic A phase.

The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (figure 1) exhibits rising tendency of smectic–isotropic transition temperatures.

Gray[20] has explained the rising tendency of transition temperatures in low melting homologous series. Addition of each methylene group increases the polarizability and the length of the molecules which rises the mesomorphic-isotropic transitions. Gray[20] has also explained the effect of lateral methyl group on mesomorphism. A lateral methyl group generally lowers the transition temperatures. Reference to figure 1 indicates that a sharp decrease in solid to mesomorphic transitions in the middle members is reponsible for the enantiotropic transition in the present series. However, in higher homologues, solid to mesomorphic transition temperatures exhibiting rising tendency.

Table 4 summarizes the average thermal stabilities and comparative geometry of the present series (**1**) and the structurally related series A[16], B[16] and C[10]. The average smectic thermal stability of series I is lower than that of series A and series B. Molecules of series **1** differ from series A and B only in the terminal linkage at one end. Molecles of series **1** have an additional –C=C(CH$_3$)– linkage at the terminus which makes the molecule a little longer and more polarizable as compared to molecules of series A and B. However, the *trans a*-methyl group of series **1** contributes towards the increase in the breadth of the molecules. It has been observed that increase in the breadth of the molecules adversely affects the smectic phase compared to the nematic phase. It seems that the thickening effect[20] caused by the *a*-methyl group has out balanced the effect of increased length and polarizability of molecules of series **1** by reducing its average smectic thermal stabilities.
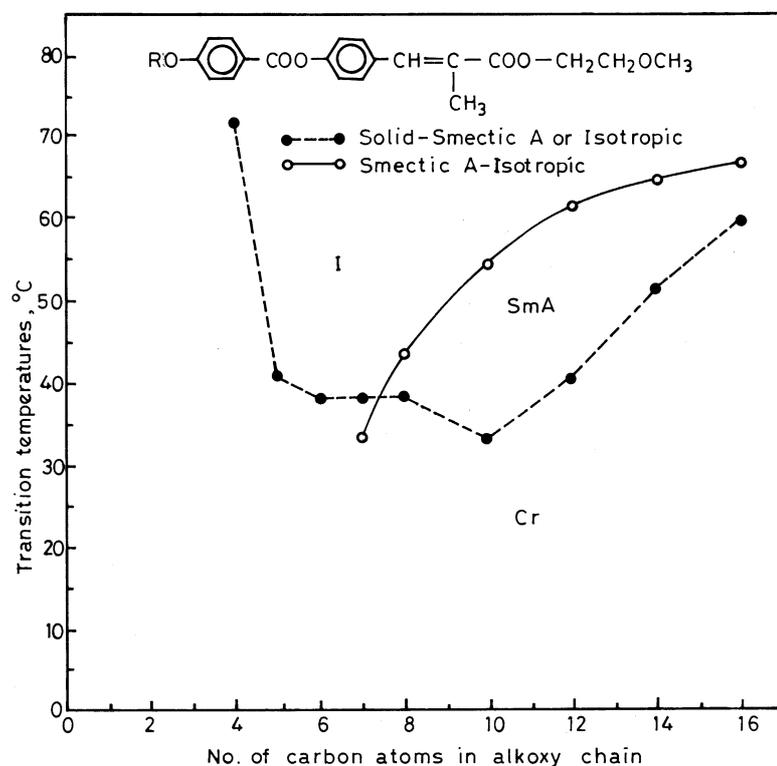
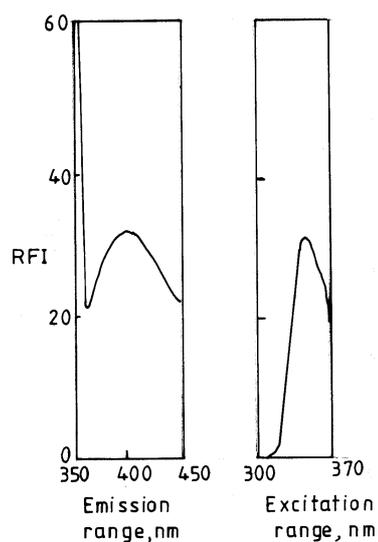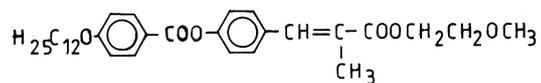

Figure 1.   Phase behaviour of series **1**.

Reference to table 4 indicates that the average smectic thermal stability of series **1** is lower than that of series C. Molecules of series C have *n*-butyl ester linkage at one terminus against the broken alkoxy terminus in the molecules of series **1**. Moreover,

Table 4. Average thermal stabilities (°C).

$$RO-\bigcirc-COO-\bigcirc-CH=\underset{\underset{CH_3}{|}}{C}-COOCH_2CH_2OCH_3 \qquad \text{Series } \mathbf{1}$$

$$RO-\bigcirc-COO-\bigcirc-COOCH_2CH_2OCH_2CH_3 \qquad \text{Series } \mathbf{A}$$

$$RO-\bigcirc-COO-\bigcirc-COOCH_2CH_2OCH_3 \qquad \text{Series } \mathbf{B}$$

$$RO-\bigcirc-CH=CH-COO-\bigcirc-COOCH_2CH_2CH_2CH_3 \qquad \text{Series } \mathbf{C}$$

Comparative geometry of series **1**, **A**, **B** and **C**.

Series	1	A	B	C
Smectic to isotropic (C_7–C_{16}) –	53·5	56·33	66·33	106·17
commencement of smectic phase	C_7	C_5	C_5	C_2

$$H_{25}C_{12}O-\bigcirc-COO-\bigcirc-CH=\underset{\underset{CH_3}{|}}{C}-COOCH_2CH_2OCH_3$$

Figure 2. Fluorescence spectra of compounds (**1**).

molecules of series C have a cinnamoyl group as a central linkage, which has no lateral *a*-methyl group, whereas molecules of series **1** have lateral *a*-methyl group on the cinnamoyl linkage at the terminus. All these factors enhance the smectic thermal stability of series C compared to series **1**, which is the case.

3.1 *Fluorescent study*

The benzene ring with its six **p**-electrons can act in conjunction with electron-donating groups (auxochromes like –NH$_2$, RHN–, R$_1$R$_2$N–, –O–, –OH, –OR etc.) and electron-accepting groups (like –CN, –C=C–, –CO– etc.) to produce strong absorption in the UV or visible regions which may give rise to fluorescence. Earlier Chudgar *et al* reported esters[21] and benzopyran-4[H] one heterocyclic[22] mesogenic derivatives exhibiting fluorescent properties. With this in view, *n*-dodecyloxy derivatives of series **1** were studied for their fluorescent properties. Excitation and emission spectra were recorded for the compound on a Shimadzu Rf 540 spectrophoflurometer at room temperature. The excitation spectra are records of luminescence intensity at fixed emissions as functions of the excitation wavelength. Fluorescence emission spectra are those in which excitation wavelength is kept constant and the corresponding wavelength distribution of the emitted radiation is measured. The excitation peak at 345 nm and the emission peak at 402 nm were observed (figure 2). This indicates that all the homologues of series **1** exhibit fluorescence property.

4. Conclusion

New mesogenic homologous series of **a**-methylcinnamates were synthesized. The study indicated that the **a**-methyl group on the cinnamoyl linkage adversely affects mesophase thermal stabilities. However the study has provided liquid crystalline compounds exhibiting smectic A phase at ambient temperature.

Acknowledgments

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