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Variation in Mesomorphic Characteristics with Certain Alterations in Molecular Structure: Homologous Series iso-Propyl *p*-(*p'*-*n*-Alkoxy Cinnamoyloxy) Benzoates and iso-Propyl *p*-(*p'*-*n*-Alkoxy Benzoyloxy) Benzoates

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Mesomorphic characteristics of homologous series *n*-propyl *p*-(*p'*-*n*-alkoxy cinnamoyloxy)benzoates (I)¹ are quite in keeping with the general molecular structure and molecular forces accruing therefrom. Continuing the work further, the right hand terminal group of the series (I) has been replaced by a branched group with iso disposition of the alkylchain but having the same number of carbon atoms. Thus the new homologous series iso-propyl *p*-(*p'*-*n*-alkoxy cinnamoyloxy)benzoates (II) with all other molecular geometry the same, gets mesomorphic characteristics changed considerably. The first few members become non-mesogenic, nematic orientation is altogether eliminates and the smectic mesophase range is reduced to about one third of that of the series (I). Another new homologous series (III) with all the molecular geometry of the series (II), but with a shorter central bridge —COO— than —CH=CH—COO— receives a further jolt in its exhibition of mesomorphic characteristics. The first seven members and the last member of the series (III) become non-mesomorphic; however, some middle members exhibit monotropic smectic mesophase. The effect of the branching of the terminal substituent and shortening of the central bridge are thus quite evident and arouse good interest. The smectic texture as determined by optical microscopy and by the study of mixtures² is of fan shaped focal conic smectic A variety.

INTRODUCTION

Molecular structure and forces arising therefrom are known to modify liquid crystalline properties. With the alterations in molecular geometry of a mesogen, the liquid crystallinity may be, favourably or adversely, affected depending upon the nature of the changes made. Such a study normally makes it possible to attribute the changes both in molecular structures and mesomorphic characteristics to each other, besides opening newer possibilities for appropriate relationship. In this investigation, two new homologous series have been synthesized by changing either a terminal substituent or a central bridge of a mesomorphic homologous series¹ while maintaining the long nature of its molecules along with their usual aromaticity.

EXPERIMENTAL

Synthesis and study

1. *p-n-Alkoxy benzaldehydes* were prepared from *p*-hydroxy benzaldehydes.³
2. *trans-p-n-Alkoxy cinnamic acids* were synthesized from *p-n*-alkoxy benzaldehydes.⁴

TABLE I
Transitions iso-Propyl *p*-(*p'*-*n*-alkoxy cinnamoyloxy)benzoates

No.	No. of carbon atoms in the —OR groups of the compound	Smectic	Transitions °C	
			Nematic	Isotropic
1	C ₁	—	—	98.0
2	C ₂	—	—	122.0
3	C ₃	—	—	124.0
4	C ₄	(98.0)	—	106.0
5	C ₅	(95.0)	—	112.0
6	C ₆	(98.0)	—	108.0
7	C ₇	(91.5)	—	95.0
8	C ₈	92.0	—	95.5
9	C ₁₀	79.0	—	92.0
10	C ₁₂	82.0	—	91.5
11	C ₁₄	79.0	—	92.0
12	C ₁₈	(102.0)	—	107.0

Values in parenthesis indicate monotropic transitions.

3. *trans-p-n-Alkoxy cinnamoyl chlorides* were synthesized from *trans p-n*-alkoxy cinnamic acids.⁵

4. *iso-Propyl p-hydroxy benzoates* were prepared from isopropyl alcohol and *p*-hydroxy benzoic acid.⁶

5. *iso-Propyl p-(p'-n-alkoxy cinnamoyloxy) benzoates*:

iso-Propyl p-hydroxy benzoate (0.01 mole) was dissolved in dry pyridine (10.0 ml) and added slowly to the corresponding *trans-p-n*-alkoxy cinnamoyl chlorides (0.015 mole). The mixture was warmed while shaking for an hour and was allowed to stand overnight. It was then acidified with cold dilute hydrochloric acid. The precipitated ester was collected by filtration and washed with water followed by cold dilute sodium hydroxide solution. After giving a rewash with water, the crude ester was crystallized from ethyl alcohol: ethyl acetate (80 : 20) mixture. The transitions are recorded in Table I. The elemental analysis conforms with the calculated ones.

6. *p-n-Alkoxy benzoic acids* were prepared from *p*-hydroxy benzoic acids.⁷

7. *p-n-Alkoxy benzoyl chlorides* were prepared from *p-n*-alkoxy benzoic acids.⁸

8. *iso-Propyl p-(p'-n-alkoxy benzoyloxy)benzoates*:

These were prepared from *iso-Propyl p-hydroxy benzoates* (0.01 mole) and corresponding *p-n*-alkoxybenzoyl chlorides (0.015 mole) in the same way as described in 5 above. The transitions are recorded in Table II. The elemental analysis conforms with the calculated ones.

TABLE II

Transitions *iso-Propyl p-(p'-n-alkoxy benzoyloxy)benzoates*

No.	No. of carbon atoms in the —OR group of the compound	Smectic	Transitions °C	
			Nematic	Isotropic
1	C ₁	—	—	75.0
2	C ₂	—	—	97.5
3	C ₃	—	—	91.0
4	C ₄	—	—	85.0
5	C ₅	—	—	93.0
6	C ₆	—	—	89.0
7	C ₇	—	—	73.5
8	C ₈	(57.0)	—	58.0
9	C ₁₀	(56.0)	—	62.5
10	C ₁₂	(55.0)	—	65.0
11	C ₁₄	(52.0)	—	75.0
12	C ₁₈	—	—	76.0

Values in parenthesis indicate monotropic transitions.

The mesomorphic characteristics of both homologous series have been studied by optical microscopy and by the system of mixtures.

RESULTS AND DISCUSSION

The transitions of both homologous series are plotted against the number of carbon atoms of the alkyl chain at the left end of the molecules (Figures 1 and 2). A contrast in the nature of the transition curves is quite evident.

Lohar and Mashru¹ studied the mesomorphic characteristics of the homologous series (I) *n*-Propyl *p*-(*p'*-*n*-alkoxy cinnamoyloxy)benzoates. It was designed to replace the straight chain propyl group by a branched isopropyl substituent, as well as the longer central bridge —CH=CH—COO— by a shorter —COO— group, in a stepwise manner. Thus two new homologous series (II) iso-Propyl *p*-(*p'*-*n*-

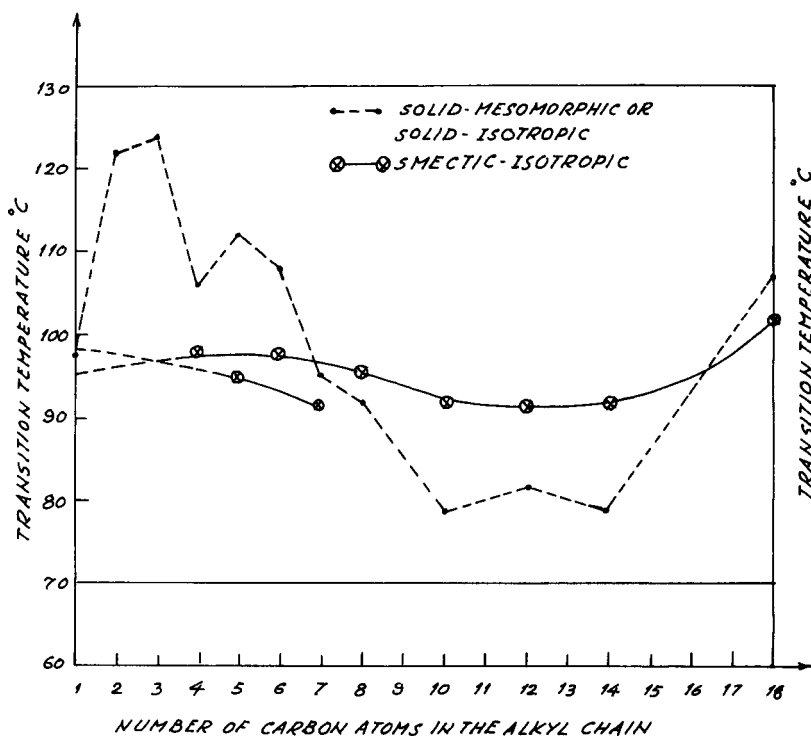
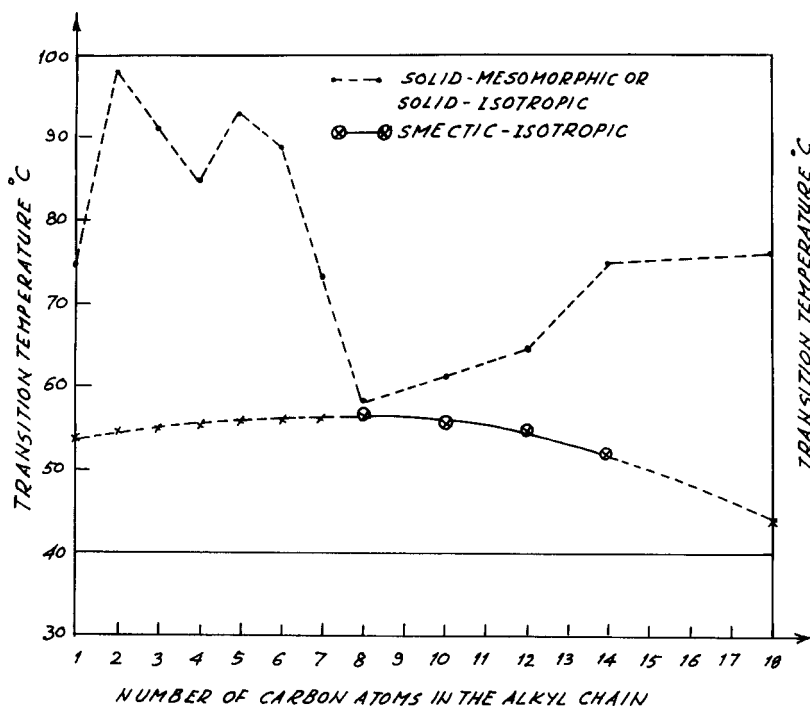
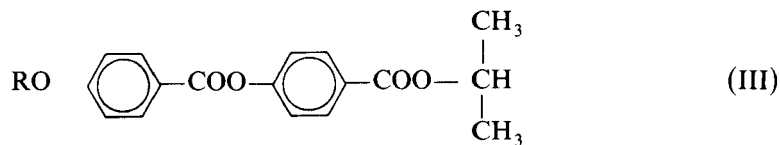
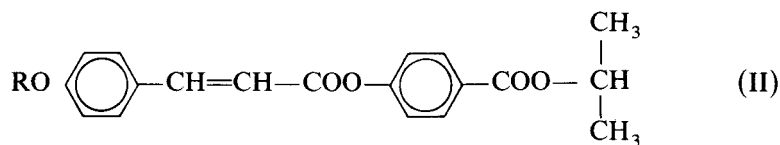
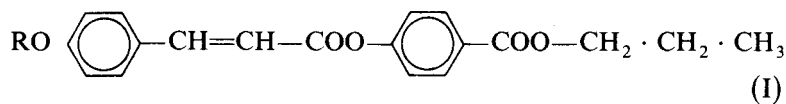


FIGURE 1 iso-Propyl *p*-(*p'*-*n*-alkoxycinnamoyloxy)benzoates

FIGURE 2 iso-Propyl *p*-(*p'*-*n*-alkoxybenzoyloxy)benzoates

alkoxy cinnamoyloxy)benzoates and (III) iso-Propyl *p*-(*p'*-*n*-alkoxy benzoyloxy)benzoates, each with twelve compounds were synthesized. Their molecular geometry may be depicted as follows:-



where R represents alkyl chain with carbon atoms varying from C₁ to C₈ and C₁₀, C₁₂, C₁₄ and C₁₈ (II & III) and C₁ to C₈ and C₁₀, C₁₂, C₁₆, and C₁₈ (I).

The mesomorphic characteristics of the homologous series (I)¹ are quite rich. The first homologue is a nematogen; polymesomorphism begins from the second member, though in this and the third member the smectic property is exhibited in monotropic condition, and continues up to the fifth homologue. The homologues sixth and beyond show purely smectic property. The series is predominantly smectogenic and low melting and shows mesomorphic range varying from about 20° to about 42° C.

Comparison of the mesomorphic characteristics of the series (II) with those of series (I)¹ reveal interesting variations. With only one specific change brought in at the right terminal group of the series (I), the first three members of the homologous series (II) iso-Propyl *p*-(*p*'-*n*-alkoxy cinnamoyloxy) benzoates (Figure 1 and Table I) turn out to be non-mesogens though they melt at moderate temperatures. The nematic property shown by the series (I) is altogether eliminated in the case of series (II). Perhaps very high crystallizing tendency does not permit its exhibition even in monotropic condition. Polymesomorphism *thus* is *this* eliminated with *n*-propyl linking (I) changing into isopropyl linking (II). The next four members of the series (II), from the fourth to the seventh homologue (Figure 1), exhibit smectic property in monotropic condition versus the second and third members of the series (I).¹ Enantiotropic smectic mesophase (series II) makes its appearance at the eighth homologue and continues to be exhibited up to the fourteenth member with the indication, as conveyed by the smooth nature of the smectic-isotropic transition curve (Figure 1) that the sixteenth member could be an enantiotropic smectogen. With the alteration in the geometry of the right terminal substituent, the mesomorphic range of the series (II) is reduced by about one third of that of series (I) with reference to the middle octyl homologue in both series, making the octadecyl member (series II) again a monotropic smectogen, against its counter part of series (I) which has a good enantiotropic smectic range of about 30° C.¹ The smectic-isotropic transitions of the series (II) are also lowered to a considerable extent as compared to those of the series (I).¹ Despite this striking contrast, a point of resemblance is the rare⁹ alternation effect in the smectic transitions, though with a difference. In the case of series (I)¹ with the straight propyl linking the smectic-nematic transitions show a rare but clear alternation effect. The present homologous

series (II) also where the corresponding propyl linking is branched in the iso style, retains the rare smectic odd-even effect (Figure 1).

With the branched linking of the propyl sector of the ester group at the right terminal (series II) the overall breadth and thickness of the molecules will be partially increased with a slight reduction in the length as compared to the molecules of series (I).¹ One methyl unit in the iso position will fall off¹⁰ the main axis forcing the long axis of the molecules apart and introducing intra molecular steric effect. While the over all polarizability of the molecules of both series would be quite comparable, the enhanced breadth and thickness of the molecules of the series (II) along with the induced steric hindrance should be taken as directly responsible for the degradation in the mesomorphic characteristics since the resistance against the thermal agitation would go down.

The molecules of the homologous series (III) iso-Propyl *p*-(*p'*-*n*-alkoxy benzyloxy)benzoates have a shorter central bridge —COO— with less delocalized electrons as compared to the molecules of the series (II) with the vinylcarboxyl central bridge. Thus the molecules of the series (III) would be endowed with less polarizability than those of the series (II). This becomes a sufficient cause for further degradation in the mesomorphic characteristics. Now, the first seven members of the series (III) are forced to shed, the mesomorphic character and become ordinary members of the homologous series though the isotropic liquid transitions are very moderate (Figure 2). Enantiotropic smectic mesomorphic property too is altogether lost with the elimination of the nematic property. Elimination of nematic property may be quite natural since the enhanced breadth of the molecules and the breadth to length ratio would not be conducive to its exhibition. The octadecyloxy member becomes a non-mesogen. The eighteenth member of the series (I), (II) and (III) show a gradual degradation from an enantiotropic smectic mesophase of about 30°C range to a monotropic smectic range of about 5°C and non-mesogenic character in the same sequence. Only the octyl, dodecyl and tetradecyl members of the series (III) show smectic mesophase in monotropic condition. There is an indication, for the hexadecyl derivative to be a monotropic smectogen. In other words, with decreased polarizability, the smectic property is forced into monotropy, that too by just four (or five) middle and later members making the degradation in the mesomorphic characteristics almost complete (III).

Thermal stabilities of these three homologous series are given in Table III. It is observed that with the branching off of the propyl

TABLE III
Thermal stabilities °C

Series	I	II	III
Smectic-Isotropic	119.0 (C ₈ -C ₁₂)	93.0 (C ₈ -C ₁₂)	56.0 (C ₈ -C ₁₂)
Commencement of Smectic Mesophase	C ₂	C ₄	C ₈

linking in iso form at the right terminal, the average smectic-isotropic thermal stability is decreased by 26° and with shortening of the central bridge and proportionate decrease in its π electron density, the average smectic-isotropic thermal stability is further decreased by 37°. Commencement of smectic mesophase is also affected in a similar manner; it begins at the second member in the series (I), but from the fourth member in series (II) and the eighth member in series (III). The smectic texture of the homologues of both series as discerned from optical microscopy as well as the method of mixtures² is that of fan shaped focal conic smectic A variety.

In conclusion the mesomorphic influence declines with straight linking of alkylchain changed to iso form, as revealed from this study. Iso disposition of the alkyl chain results into decrease in smectic thermal stability as compared to that due to a straight chain form. Shorter central bridge further decreases the thermal stability appreciably.

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