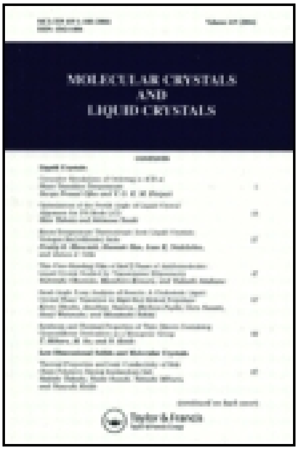

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Mesomorphic Characteristics of Thermotropic Mesogens *p*-*p*′-Disubstituted Phenyl Cinnamates I: *p*-(*p*′-*n*-Alkoxycinnamoyloxy)-Acetophenones†

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p-*n*-Alkoxycinnamoyl chlorides when treated with *p*-hydroxyacetophenone yield a homologous series of mesogens. The first member is a monotropic nematogen; exhibition of enantiotropic nematic mesophase begins from the second member and persists up to the butyl derivative. Both smectic and nematic mesophases are exhibited by the pentyl and hexyl derivatives. The homologues from heptyl to octadecyl exhibit smectic phase only. The usual odd-even effect is well displayed. Nematic-isotropic transition curves for both even and odd members show an initial slight slump up to the heptyl derivative; the smectic-isotropic transition curve shows a rising tendency followed by a slight downward slope towards the highest member. The homologous series is thermally very stable and exhibits a wide mesomorphic range. The thermal stabilities and other characteristics are discussed.

INTRODUCTION

Liquid crystals have received a thrust which is quite understandable in view of their increasing utility. Obviously, the search for new liquid crystalline substances will receive a similar impetus. In this investigation a new homologous series of mesogens has been synthesized and its mesomorphic characteristics have been determined. A comparative assessment of their characteristics with those of similar other homologous series has also been attempted.

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EXPERIMENTAL

Preparation of the homologues

1) *p*-*n*-Alkoxy benzaldehydes: These are prepared by the method of Vyas and Shah.[2]
2) trans-*p*-*n*-Alkoxy cinnamic acids: These are prepared from the corresponding *p*-*n*-alkoxy benzaldehydes and malonic acid.[3]
3) trans-*p*-*n*-Alkoxy cinnamoyl chlorides: These are prepared from corresponding trans-*p*-*n*-alkoxy cinnamic acids and thionyl chlorides.[4]
4) Preparation of the esters: *p*-(*p*′-*n*-Alkoxy cinnamoyloxy)acetophenones: *p*-(*p*′-*n*-Allkoxy cinnamoyloxy)acetophenones are synthesized by reacting trans-*p*-*n*-alkoxy cinnamoyl chlorides with *p*-hydroxy acetophenone.

Dry *p*-hydroxy acetophenone (0.01 mole) is dissolved in dry pyridine (A.R. 10 ml.) and is added to the trans-*p*-*n*-alkoxy cinnamoyl chloride (0.015 mole). The mixture is warmed while shaking for an hour and is allowed to stand overnight. It is acidified with cold dilute hydrochloric acid and the precipitates are collected by filteration and are washed with cold dilute sodium hydroxide solution followed by water. The solid esters are crystallized from dilute ethanol. The transitions are compiled in Table I. The elemental analytical data for all the homologues are in conformity with the calculated ones.

TABLE I

p-(*p*′-n-Alkoxycinnamoyloxy)acetophenones

	Transition temperatures (°C)		
n-Alkyl group	Smectic	Nematic	Isotropic
1. Methyl	—	(137.0)†	149.0
2. Ethyl	—	142.0	143.5
3. Propyl	—	126.5	133.0
4. Butyl	(102.5)‡	113.5	141.0
5. Pentyl	100.5	117.0	133.0
6. Hexyl	104.0	126.0	136.5
7. Heptyl	101.5	—	133.0
8. Octyl	95.0	—	138.0
9. Decyl	100.0	—	141.0
10. Dodecyl	102.5	—	141.0
11. Hexadecyl	111.0	—	141.0
12. Octadecyl	105.0	—	137.0

† Value in the parenthesis indicates monotropy.
‡ Value obtained by extrapolation.

RESULTS AND DISCUSSION

The nematic property is exhibited from the very first member of *p*-(*p*′-*n*-alkoxycinnamoyloxy)acetophenone series, though of monotropic variety. The first member seems to be unable to resist the strong thermal vibrations at high temperatures and yields suddenly an unoriented isotropic liquid. On cooling this isotropic liquid, supercooling persists below solid-isotropic point, and the molecules which apparently possess all the prerequisites for exhibiting mesomorphism get their chance of setting themselves to a threaded orientation, before the liquid is crystallized, giving rise to monotropic nematic phase. In a parallel homologous series viz. *p*-(*p*′-*n*-alkoxybenzoyloxy)acetophenones[1] with smaller carboxy, —COO—, central group, the first three compounds are found to be non-mesomorphic, though the series is a low melting one. The monotropic nematic phase is exhibited from the fourth to the sixth members in case of this series.[1] The increased length of the vinyl carboxy, —CH=CH—COO, central group in the present cinnamoyloxy series is responsible for enhancing the transitions as well as early beginning of mesomorphism since the overall polarizability of the molecules gets enhanced.

The solid mesomorphic curve (Figure 1) of the homologous series *p*-(*p*′-*n*-alkoxycinnamoyloxy)acetophenones indicates a steep fall up to the eighth member with slightly higher values for the sixth and seventh homologues than that of the fifth derivative. Beyond the eighth derivative the curve shows a somewhat upward trend which again falls in the case of the eighteenth member. This extraordinary fall in solid-mesomorphic transition curve provides the series with an extremely broad range of mesomorphic property, as compared to the mesomorphic range of *p*-(*p*′-*n*-alkoxybenzoyloxy)acetophenones series.[1]

Enantiotropic nematic mesophase is exhibited from the second member onwards in *p*-(*p*′-*n*-alkoxycinnamoyloxy)acetophenone series. The fifth and sixth members are polymesomorphic showing both enantiotropic smectic and nematic phases. From heptyloxy onwards up to octadecyloxy members, only smectic mesophase is exhibited. The π electron density and an added double bond at the central group coupled with the increase in polarizability due to increase in length of the alkyl chain at the terminals of the linear compounds help the smectic phase to show up.

The plot of transition temperatures versus the number of carbon atoms in the alkyl chain shows the usual odd-even effect. Nematic-isotropic transition curves for both even and odd members of this series show an initial slight slump up to the heptyl homologue. The smectic-isotropic transition curve shows a rising tendency followed by a slight downward slope towards the higher homologues.

The smectic-nematic transition curve shows a steep ascending order from the fifth to the seventh homologues. A smooth extrapolation of the curve indi-

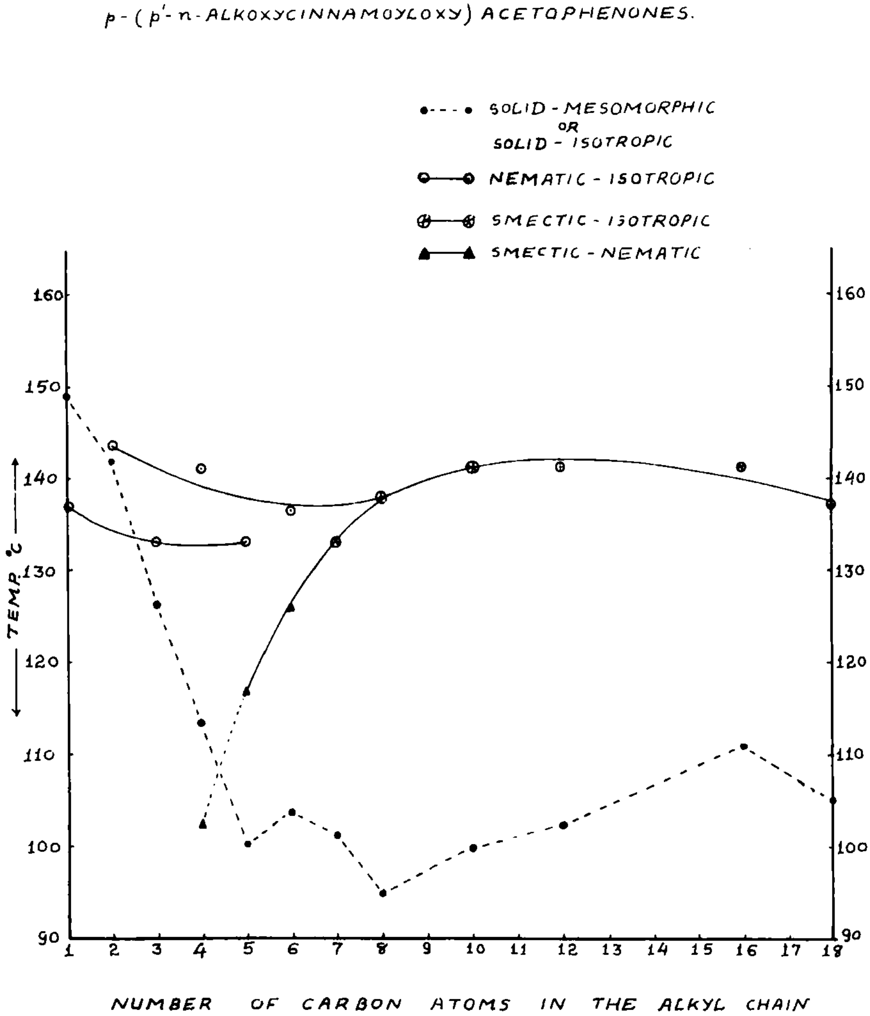


FIGURE 1 Plot of the transitions versus number of carbon atoms.

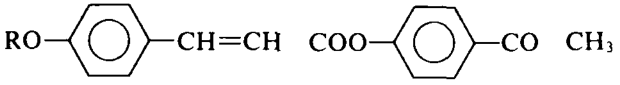
cates a temperature 102.5°, for the fourth homologue at which at least a monotropic smectic phase should have been visible but it is not observed due to the high crystallizing tendency of the homologue. The nematic-isotropic transition curve for the even homologues when joined with the smectic-isotropic points of the higher members yields a faint appearance of the wave. If this is extrapolated on the left side it indicates a temperature which is exactly the solid-isotropic point for the first number, which clearly indicates that had the compound been able to resist a little more of the thermal vibration at and above

150°, the first member could have been an enantiotropic mesomorph. Under such a possibility the transition curve for the odd member would have been nearer the transition curve for the even members giving rise to a possibility of merging the two curves at the heptyl level. The smectic-nematic and smectic-isotropic curve rises steeply reaching a maximum afterwhich a smooth fall is traced as the series is ascended. The nematic phase is of threaded texture while the smectic phase is of focal conic fan shaped Sm-A variety.

High transition temperatures are as expected due to hydrogen bonding leading to the formation of dimers in case of trans-*p*-*n*-alkoxy cinnamic acids. Esterification of these acids eliminates hydrogen bonding and yields cinnamic acid esters with lower transitions and thermal stability. However, these are somewhat higher than those for the *p*-alkyl phenyl trans-*p*′-*n*-alkoxy cinnamates.[6] Very strong terminal attractions can prevail in the case of the acetyl group attached to the other terminal of the linear molecule as compared to the alkyl group in a similar position affecting the ratio of lateral to terminal attractions and consequently resulting into a relatively high melting series of homologues.

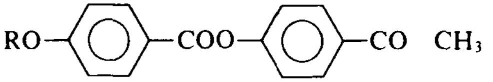
The present homologous series has been compared with other homologous series (Figure 2) for their molecular characteristics and thermal stabilities. The calculated values of average thermal stabilities are given in Table II.

The average smectic-isotropic or smectic-nematic thermal stabilities for the homologous series (1) are higher than those for the series (*K*) and (*C*); the longer vinyl carboxy group with an added double bond in case of series (1) will account for the comparatively higher average thermal stabilities since the overall polarizability of molecules is enhanced increasing the predominance of lateral attractions. However, the biphenyl unit in case of series (*V*) ob-



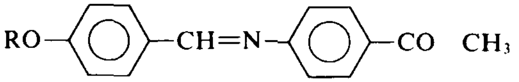
(1)

p-(*p*′-*n*-Alkoxy cinnamoyloxy)acetophenones.



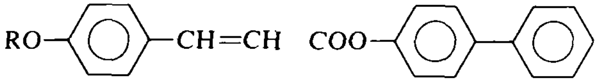
(*K*)[1]

p-(*p*′-*n*-Alkoxy benzoyloxy)acetophenones.



(*C*)[5]

p-*n*-Alkoxy benzylidene *p*′-amino acetophenones.



(*V*)[4]

p-(*p*′-*n*-Alkoxy cinnamoyloxy) biphenyls.

FIGURE 2 Homologous series under comparison.

TABLE II

Average thermal stabilities (°C).

Series	1	*K*	*C*	*V*
Nematic-Isotropic	135.8 (C_3—C_6)	88.2 (C_5—C_7)	112.7 (C_5—C_6)	206.0 (C_1—C_4)
Smectic-Nematic or Smectic-Isotropic	139.6 (C_8—C_{18})	100.1 (C_{12}—C_{18})	120.0 C_{12}—C_{14})	148.8 (C_8—C_{18})
Commencement of Smectic-mesophase	C_5	C_5	C_3	C_7

viously contributes to the lateral attractions in a larger measure as compared to the acetyl group of series (*V*) to assume higher values than those for series (1). The average nematic-isotropic thermal stabilities also follow the same pattern; that of series (1) with respect to series (*K*) and (*C*) is higher, and lower as compared to that for series (*V*), which accounts for the behavior being the same. However, the nematic thermal stabilities are lower than the corresponding smectic thermal stabilities since the lateral forces predominate over the terminal ones. The relatively greater non-coplanarity in case of the series (*K*) molecules will explain their lesser thermal stabilities as compared to those for the series (*C*) molecules.

While the commencement of smectic mesophase is comparable as far as series (1) and (*K*) are concerned, the somewhat early commencement in case of series (*C*) can be seen as due to relatively greater predominance of lateral attractions in its case and considerably late beginning in case of series (*V*) homologues as a result of the greater aromaticity on account of the biphenyl unit at the other terminal.

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