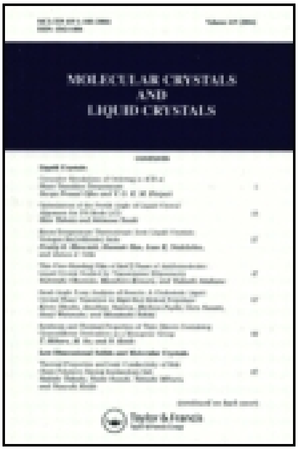

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis and Study of New Mesogens II: p-(p′-n-Alkoxycinnamoyloxy)-benzylidene p″ -anisidines (1) and p-(p′-n-Alkoxycinnamoyloxy)-benzylidene anilines (2)

J. M. Lohar [a] & J. S. Dave Jr. [a]

[a] Applied Chemistry Department, Faculty of Technology and Engineering, M. S., University of Baroda, Baroda, 390 001, India

To cite this article: J. M. Lohar & J. S. Dave Jr. (1981): Synthesis and Study of New Mesogens II: p-(p′-n-Alkoxycinnamoyloxy)-benzylidene p″ -anisidines (1) and p-(p′-n-Alkoxycinnamoyloxy)- benzylidene anilines (2), Molecular Crystals and Liquid Crystals, 70:1, 279-287

To link to this article: http://dx.doi.org/10.1080/00268948108073594

Mol. Cryst. Liq. Cryst., 1981, Vol. 70, pp. 279–287
0026-8941/81/7001-0279 $06.50/0

Printed in the United States of America

Synthesis and Study of New Mesogens II: *p*-(*p*′-*n*-Alkoxycinnamoyloxy)-benzylidene *p*″-anisidines (1) and *p*-(*p*′-*n*-Alkoxycinnamoyloxy)-benzylidene anilines (2)†

J. M. LOHAR and J. S. DAVE, Jr.

Applied Chemistry Department, Faculty of Technology and Engineering,
M. S. University of Baroda, Baroda 390 001, India.

(*Received September 18, 1980*)

Two new homologous series of liquid crystals viz. *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzylidene *p*″-anisidines (1) and *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzylidene anilines (2) comprising twenty four mesogens have been synthesized. Both are high melting series of mesomorphs. In the homologous series (1) the nematic mesophase is exhibited from the very first member; however, the first five compounds decompose at high temperatures before passing into isotropic liquid condition. Polymesomorphism is exhibited with the appearance of the smectic mesophase at the octyl derivative and remains up to the last viz. octadecyl homologue. Within polymesomorphic region the nematic mesophase is homeotropic; however, it shows a clear threaded texture where it is the only mesophase shown i.e. in the first seven members of the homologous series (1). The smectic mesophase shows focal conic fan shape texture belonging to smectic-A variety. The nematic-isotropic curve shows descending tendency as the series is ascended—a characteristic of high melting series. The smectic-nematic transition curve rises steeply and shows a levelling off tendency at the octadecyl derivative. In the homologous series (2), no decomposition occurs. The smectic mesophase commences a little early i.e. from hexyl derivative; while polymesomorphism is clearly exhibited up to the dodecyl derivative, the last two homologues are purely smectogens. The usual odd–even effect is observed in case of the nematic-isotropic curve for series (2). The smetic-nematic curve rises gradually and seems to be merging with the falling nematic-isotropic curve at the fifteenth homologue. The mesomorphic ranges in both series are quite wide; however, that of series (1) is wider than one obtained in series (2). Thermal stabilities are good and are in keeping with the molecular characteristics. The textures of the smectic and nematic mesophases are similar to that of the series (1). Both series are comparable with each other and other related series.

INTRODUCTION

Several homologous series of compounds have been found to exhibit mesomorphism whose existence has been attributed to their molecular geometry

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† Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

and the play of molecular forces arising therefrom. Thermotropic liquid crystals exhibit peculiarities as based on temperature variations which in turn are correlated with terminal and lateral substituents in the long linear molecules. Of the many, quite a few of the homologous series have ester linkages and azomethine group as central bridges besides two or more benzene rings.[1-7] Continuing our search in this field we have attempted to synthesize some new compounds forming two homologous series with no terminal substituent or a highly polar terminal substituent such as —OCH_3 to study the variations obtained in the mesomorphic characteristics.

EXPERIMENTAL

Preparation of the homologues

1) *p-n*-Alkoxy benzaldehydes: These are prepared by the method of Vyas and Shah.[8]

2) Trans-*p-n*-alkoxy cinnamic acids: These are prepared from the corresponding *p-n*-alkoxybenzaldehydes and malonic acid.[9]

3) Trans-*p-n*-alkoxy cinnamoyl chlorides: These are prepared from the corresponding trans-*p-n*-alkoxy cinnamic acids and thionyl chloride.[10]

4) *p*-(*p'-n*-Alkoxycinnamoyloxy)benzaldehydes: These are prepared by reacting trans-*p-n*-alkoxycinnamoyl chlorides with *p*-hydroxy benzaldehyde.[11]

5) Preparation of Schiffs base esters.

1) p-(p'-n-Alkoxycinnamoyloxy)benzylidene p''-anisidines These are prepared by condensing *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehydes with *p*-anisidine. Equimolar amounts (0.01 mole) of corresponding *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehyde and *p*-anisidine are refluxed for two to three hours in 20 to 25 ml ethanol containing a few drops of acetic acid. The products are crystallized from benzene:ethyl alcohol (20:80) mixture. The transitions are compiles in Table I. Elemental analytical data for all the homologues conform with the calculated ones.

2) p-(p'-n-Alkoxycinnamoyloxy)benzylidene anilines These are prepared by condensing *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehydes with redistilled aniline. Equimolar amounts (0.01 mole) of corresponding *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehyde and aniline are refluxed for two to three hours in 20 to 25 ml ethanol containing a few drops of acetic acid. The products are crystallized from benzene:ethyl alcohol (20:80) mixture. The transitions are compiled in Table II. The elemental analytical data for all the homologues conform with the calculated ones.

TABLE I

Transitions: Series (1). *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene *p*″-anisidines

n-Alkyl group	Transition Temperatures (°C) Smectic	Nematic	Isotropic
Methyl	—	162.0	301.0(D)
Ethyl	—	137.0	303.0(D)
Propyl	—	140.5	282.5(D)
Butyl	—	125.0	291.0(D)
Pentyl	—	116.5	283.0(D)
Hexyl	—	123.0	275.5
Heptyl	—	109.0	269.5
Octyl	96.5	99.5	265.0
Decyl	102.0	132.0	254.0
Dodecyl	105.0	150.0	241.0
Hexadecyl	110.0	176.0	225.5
Octadecyl	105.0	175.5	214.0

D = Decomposition point.

Method of study

The transitions and other characteristics are studied by the usual optical method as well as by using Kofler heating stage polarizing microscope.

RESULTS AND DISCUSSION

Both homologous series viz. (1) *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzylidene *p*″-anisidines and (2) *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzylidene anilines (Fig-

TABLE II

Transitions: Series (2). *p*-(*p*′*n*-Alkoxycinnamoyloxy)benzylidene anilines

n-Alkyl group	Transition Temperatures (°C) Smectic	Nematic	Isotropic
Methyl	—	145.0	222.0
Ethyl	—	143.0	236.5
Propyl	—	130.0	211.0
Butyl	—	130.0	214.5
Pentyl	—	123.0	205.0
Hexyl	119.0	139.5	200.0
Heptyl	110.0	149.0	193.5
Octyl	101.5	158.0	191.5
Decyl	90.0	166.0	180.5
Dodecyl	94.5	171.5	176.0
Hexadecyl	93.5	—	169.0
Octadecyl	93.5	—	164.0

ures 1 and 2) are high melting series of mesogens. In the series (1), the first five members show very sharp solid-nematic transitions at definite temperatures; however, they decompose abruptly at high temperatures without any smooth transition from the nematic to isotropic liquid. Smooth nematic-isotropic transitions occur from hexyl homologue onwards. The nematic-isotropic transition curve shows smooth descending tendency as the series is ascended—a characteristic of high melting series. Polymesomorphism commences from the

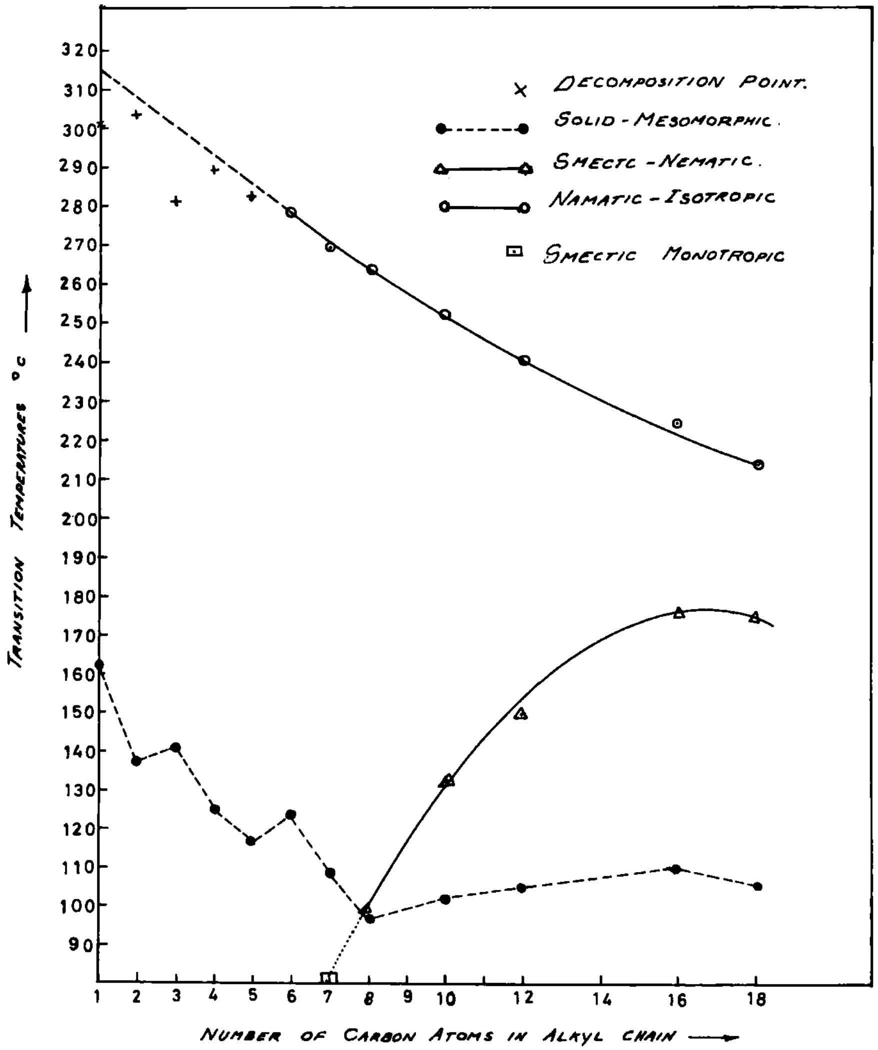


FIGURE 1 *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene *p*″-anisidines.

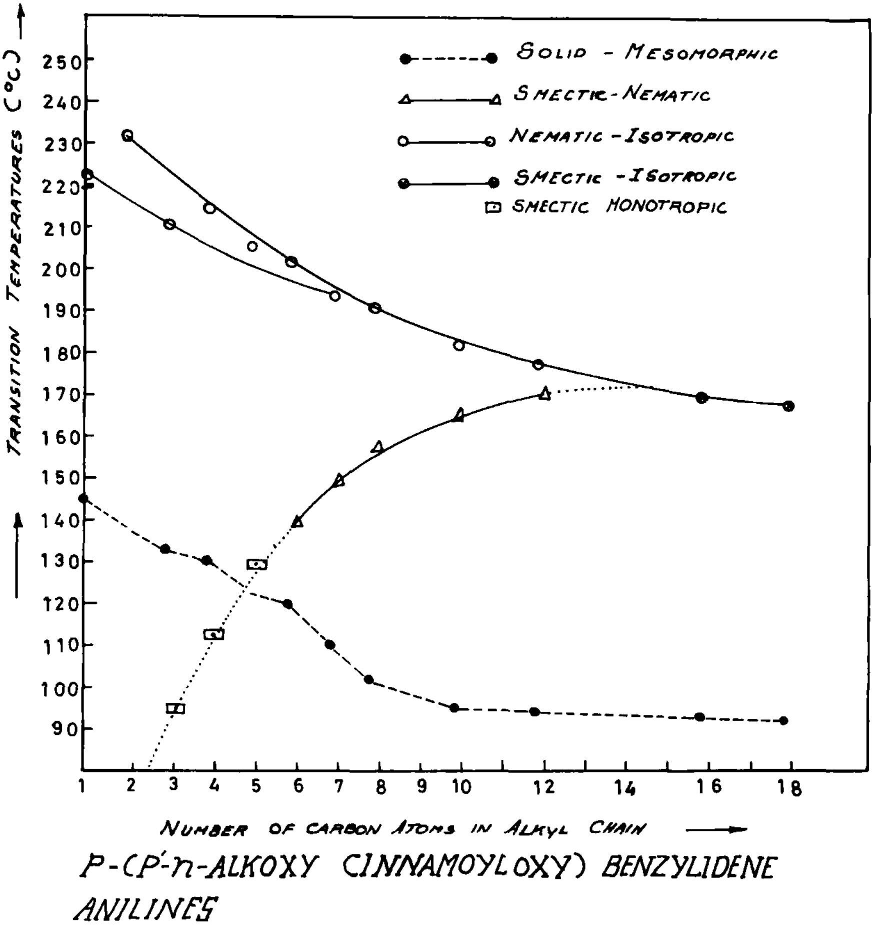


FIGURE 2 *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene anilines.

octyl member with the appearance of smectic mesophase at lower temperature and persists up to the last homologue viz. octadecyl. The smectic-nematic transition curve rises steeply as the series is ascended; however, it falls a little bit showing a levelling off tendency at the octadecyl member through hexadecyl. Due to this typicality of smectic-nematic transition curve, the smectic phase range gets enlarged at the cost of nematic mesophase which gets contracted as the series is ascended. The solid-mesomorphic curve shows a continuous overall falling tendency with intermitant rises up to eighth homologue after which it shows a rising tendency of a small range up to hexadecyloxy homologue followed by a negligible fall in its value at the octadecyloxy level. The mesomorphic range is very high which gradually decreases as the series is ascended. Within the polymesomorphic region the nematic mesophase is homeotropic i.e. from octyl derivative onwards; however, it shows a threaded texture where it is the only mesophase shown. This may be seen for the reason that as the temperature is raised reaching the smectic-nematic transition, the uniformly aligned films get their optic axis normal to the surface rendering the mesophase to adopt a homeotropic texture in the nematic phase. The smectic mesophase shows focal conic fan shaped texture belonging to A type.

In the homologous series (2), no decomposition is observed. The polymesomorphism begins somewhat early; at the hexyl derivative appearance of the smectic phase takes place. While polymesomorphism continues up to dodecyl homologue, the last two members are purely smectic. The smectic-nematic curve rises smoothly as the series is ascended and seems to be merging with the descending nematic-isotropic transition curve at the fifteenth member. The homologous series shows usual odd–even effect for nematic-isotropic curve. The solid-mesomorphic transition curve shows a gradual falling tendency up to decyl derivative after which the curve gets almost levelled off. The textures of the smectic and nematic phases are the same as shown by series (1). The mesomorphic range, though wide, is narrow as compared to the one of the series (1). On extrapolation of the smectic-nematic transition curves to the left in the case of both series (1) and (2), the values of the probable monotropic transitions for the seventh homologue (81°) (series 1) and the fifth (132°), fourth (114°) and third (94°) homologues (series 2) respectively can be obtained. These values are not realizable because of high crystallizing tendency of the mesomorphic melt on cooling the nematic liquid.

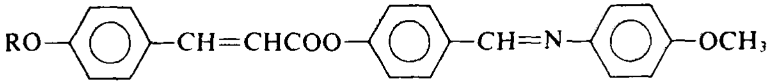
Table III shows the average thermal stabilities (°C) and the stage of commencement of the smectic phase for the following homologous series selected for comparative study.

(1) *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene *p*″-anisidines.
(2) *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene anilines.
(A) *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene *p*″-toluidines.[5]
(B) *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzylidene *p*″-phenetidines.[7]
(C) *p*-(*p*′-*n*-Alkoxybenzoyloxy)benzylidene *p*″-anisidines.[4]

TABLE III

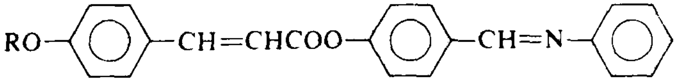
Average thermal stabilities (°C)

Series	1	2	A	B	C
Nematic-Isotropic	270.0 (C_6–C_8)	195.0 (C_6–C_8)	248.0 (C_6–C_8)	281.5 (C_6–C_8)	246.5 (C_6–C_8)
Smectic-Nematic or Smectic-Isotropic	167.2 (C_{12}–C_{18})	168.2 (C_{12}–C_{18})	190.0 (C_{12}–C_{18})	178.6 (C_{12}–C_{18})	123.4 (C_{12}–C_{18})
Commencement of smectic mesophase	C_8	C_6	C_7	C_8	C_{12}



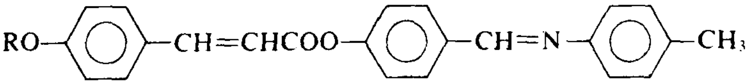
(I)

p-(*p*′-*n*-alkoxy cinnamoyloxy)benzylidene *p*″-anisidines.



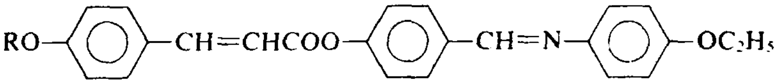
(II)

p-(*p*′-*n*-alkoxy cinnamoyloxy)benzylidene anilines.



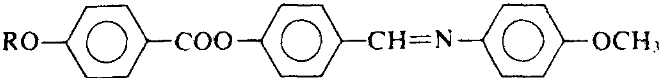
(A)[5]

p-(*p*′-*n*-alkoxy cinnamoyloxy)benzylidene *p*″-toluidines.



(B)[7]

p-(*p*′-*n*-alkoxy cinnamoyloxy)benzylidene *p*″-phenetidines.



(C)[4]

p-(*p*′-*n*-alkoxy benzoyloxy)benzylidene *p*″-anisidines.

FIGURE 3 Homologous series under comparison.

Most of the molecular geometry of all the homologous series (Figure 3) under comparison is common, the only uncommon part being the different terminal groups at one end in most of them. Besides this, in case of series (C) homologues, one of the two central bridges differs from those of all other series. Very naturally, the overall polarity and polarizability of the molecules belonging to different homologous series under comparison will be comparable including the effect due to non-coplanar nature of the molecules; thus most of the mesomorphic characteristics should also be comparable. The reasons for all the variations that arise can obviously be traced to the different terminal groups at one end and to the shorter carboxy central bridge without the double bond in case of series (C) homologues.

Nematic-isotropic thermal stability of the homologous series (2) is the lowest. It can be seen that at the other end the homologues of this series have —H as the terminal group which contributes little to the overall polarity and polarizability of the molecules in contrast to the —CH_3, —OCH_3 and —OC_2H_5 terminal groups possessed at the other end by the molecules of the other homologous series. High polarity and polarizability will enhance thermal stability. As compared to series (1) the average nematic-isotropic thermal stability of the series (B) homologues is higher for the reason that their other terminal group viz. —OC_2H_5 is more polar and lengthy than the —OCH_3 terminal group at the other end of the series (1) homologues. Nematic-isotropic thermal stabilities of series (1) and (C) also differ; while their terminal groups at the other end are also the same, the carboxy central bridge in case of series (C) attributes lesser lateral attractions than those attributed by the vinyl carboxy central bridge of series (1), causing their nematic-isotropic thermal stability to assume a lower value.

It is interesting to note that the nematic-isotropic thermal stabilities of series (A) and (C) are very near each other though their terminal groups at the other end as well as one central bridge differ. It appears that what is lost due to less polar group (—CH_3) at the other end is compensated by a longer vinyl carboxy (—CH═CH—COO) group and its double bond as one of its central bridges and hence the nematic-isotropic thermal stabilities of these two series are almost comparable. The order of nematic-isotropic thermal stability is in agreement with that derived by Gray.[12]

The case of smectic-nematic or smectic-isotropic thermal stability is somewhat different. Lateral attractions should be playing greater role in determining the smectic characteristics. However, the terminally situated dipole moments may give rise to a complicated situation because of their possible dual role in affecting both terminal and lateral attractions.[12] The lowest average smectic-nematic or smectic-isotropic thermal stability is that of series (C) where one central bridge is the carboxy group whose contribution to lateral attractions is surely less than the corresponding vinyl carboxy as the central bridge. But within the series having vinyl carboxy as one central bridge, the one with a methyl terminal group at the other end viz. series (A) has the highest smectic thermal stability. It would appear that the dipole interactions due to methyl terminal group contribute to lateral attractions more than the more polar methoxy or ethoxy terminal groups as is suggested by the smectic thermal stability values for series (1) and (B). With —H group in series (2) the smectic thermal stability is slightly more than that of series (1) where sufficiently polar methoxy group is situated at the other end. This study suggests the following order for the smectic stability which slightly differs from that given by Gray.[12]

$$CH_3 > OC_2H_5 > H > OCH_3$$

Commencement of smectic phase in the homologous series under comparison can be another reflection on the factors that contribute to the lateral attractions in the molecules. Smectic phase commences quite early at C_6 level in series (2) since the lateral attractions due to the central bridges quite predominate with almost no contribution by the terminal —H group to overall terminal attractions of the molecules. This is followed by series A, with methyl as terminal group at the other end, at the seventh homologue, and series (1) and (B), where the terminal groups at the other end are methoxy and ethoxy respectively, at the eighth homologues. The order for commencement of smectic phase, as suggested by the study of these series, can be presented as follows in terms of the terminal substituents at the other end, the order being in decreasing sequence of ealry commencement of smectic phase.

$$H > CH_3 > OCH_3 > OC_2H_5$$

Interestingly, this order is the reverse order of the mixed nematic liquid crystal formation.[13] Quite convincingly the commencement of smectic phase is as late as the twelfth member in case of series (C) since the carboxy central bridge gives rise to less lateral attractions than the vinyl carboxy central bridge.

A disappointing feature of the homologous series (1) is the decomposition of its first five members without showing any indication of smooth and sharp transitions from nematic to isotropic liquid. One is led to believe that the molecular forces behave quite typically; while they offer sufficient resistance to growing thermal agitation up to about 300°, 302°, 281°, 290°, and 282° for the first, second, third, fourth and fifth derivatives respectively, they suddenly yield to an abrupt disorder a little above, as the molecular forces above these do not seem to be adequate enough for a smooth transition to isotropic liquid. With increasing alkyl chain length in the alkoxy group at one end as the series is ascended, the overall polarizability of the molecules gets increased; thus nematic-isotropic transitions are lowered. Consequently from the hexyl homologue onwards smooth transitions occur.

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