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Schiffs Base Homologous Series of New Mesogens: p-(p′-n-Alkoxycinnamoyloxy) benzylidene-p″-N, N-Dimethylaminoanilines and p-(p′-n-Alkoxycinnamoyloxy) benzylidene-p″-N, N-Diethylaminoanilines

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Schiffs Base Homologous Series of New Mesogens: *p*-(*p'*-*n*-Alkoxycinnamoyloxy)benzylidene-*p''*-*N*,*N*-Dimethylaminoanilines and *p*-(*p'*-*n*-Alkoxycinnamoyloxy)benzylidene-*p''*-*N*,*N*-Diethylaminoanilines†

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Two new homologous series comprising vinyl carboxy, —CH=CH—COO—, and azomethine, —CH=N—, as central groups have been synthesized by treating *p*-(*p'*-*n*-alkoxycinnamoyloxy) benzaldehydes with *p*-amino *N*,*N*-dimethyl (I) and diethyl (II) anilines. All the twenty-four compounds are mesogenic in nature. Both series of liquid crystals are primarily nematogenic in character and high melting. Very wide range of mesomorphism is observed in all the homologues. In series (I) the first seven members decompose before passing into isotropic liquid form at higher temperatures because of which observation of the usual odd-even effect is missed. However, the series (II) homologues exhibit the usual odd-even effect since they do not decompose at higher temperatures. While the mesomorphic range is quite wide in series (I), that in series (II) is relatively less wide. The thermal stabilities are comparable. The special feature is that the smectic mesophase makes its appearance at very late stage; in series (I) at the hexadecyloxy stage and in series (II) at dodecyloxy derivative, all in monotropic conditions excepting the octadecyloxy homologue of the series (I) where the small enantiotropic smectic range of about 2.5°C is observed.

INTRODUCTION

Many homologous series are known with two central linkages viz. (i) ester linkage and (ii) azomethine linkage.[1-4] Some series are found to be purely smectogenic while some others show polymesomorphic character. The present two

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new homologous series with vinyl carboxy, —CH=CH—COO—, and azomethine, —CH=N—, linkages have certain important characteristics. These two new series offer good comparison in their mesomorphic properties as well as their temperature dependence with other structurally related homologous series.[5,6]

EXPERIMENTAL

Preparation of the homologues

1. *p-n*-Alkoxy benzaldehydes: These are prepared by the method of Vyas and Shah.[7]

2. Trans-*p-n*-alkoxy cinnamic acids: These are prepared from the corresponding *p-n*-alkoxy benzaldehydes and malonic acid.[8]

3. Trans-*p-n*-alkoxy cinnamoyl chlorides: These are prepared from the corresponding trans-*p-n*-alkoxy cinnamic acids and thionyl chloride.[9]

4. *p*-(*p'-n*-Alkoxycinnamoyloxy)benzaldehydes: These are prepared by reacting trans-*p-n*-alkoxycinnamoyl chlorides with *p*-hydroxy benzaldehyde.[10]

5. Preparation of the Schiffs bases: (I) *p*-(*p'-n*-Alkoxycinnamoyloxy)benzylidene *p''-N,N*-dimethylamino anilines.

p(*p'-n*-Alkoxycinnamoyloxy)benzylidene *p''-N,N*-dimethylamino anilines are prepared by condensing *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehydes with *p*-amino, *N,N*-dimethylaniline. Equimolar amounts (0.01 mole) of *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehyde and *p*-amino, *N,N*-dimethylaniline are refluxed for an hour in 20 to 25 ml ethanol containing a few drops of acetic acid. The products are crystallized from ethyl alcohol:benzene (80:20) mixture. The transitions are compiled in Table I. The elemental analytical data for all the homologues are in conformity with the calculated ones. (II). *p*-(*p'-n*-Alkoxycinnamoyloxy)benzylidene *p''-N,N*-diethylamino anilines: *p*-(*p'-n*-Alkoxycinnamoyloxy)benzylidene *p''-N,N*-diethylamino anilines are prepared by condensing *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehydes with *p*-amino, *N,N*-diethylaniline. Equimolar amounts of (0.01 mole) of *p*-(*p'-n*-alkoxycinnamoyloxy)benzaldehyde and *p*-amino, *N,N*-diethylaniline are refluxed for an hour in 20 to 25 ml of ethanol containing a few drops of acetic acid. The products are crystallized from ethyl alcohol:benzene (80:20) mixture. The transitions are compiled in Table II. The elemental analytical data for all the homologues are in conformity with the calculated ones.

Method of study

The transitions and other characteristics are studied by the usual optical method as well as under polarizing microscope.

TABLE I

Transition temperature: series I *p*(*p'-n*-Alkoxycinnamoyloxy) benzylidene *p"-N,N*-dimethylamino anilines

n-Alkyl group	Transition temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	—	194.5	279.0(D)
Ethyl	—	206.0	280.0(D)
Propyl	—	219.5	283.0(D)
Butyl	—	179.5	273.5(D)
Pentyl	—	153.5	267.0(D)
Hexayl	—	145.0	267.0(D)
Heptyl	—	138.0	257.0(D)
Octyl	—	132.0	245.5
Decyl	—	138.0	240.0
Dodecyl	—	135.0	233.0
Hexadecyl	(118.0)	132.5	218.0
Octadecyl	124.0	128.0	210.0

Value in the parenthesis indicates monotropy.
D: Decomposition temperature

RESULTS AND DISCUSSION

The homologous series *p*-(*p'-n*-alkoxycinnamoyloxy)benzylidene *p"-N,N*-dimethylamino aniline (I) is a high melting series with wide mesomorphic range and high thermal stability. The plot (Figure 1) of solid-mesomorphic transitions versus the number of carbon atoms in the alkyl chain of the alkoxy end

TABLE II

Transition temperatures: series II *p*-(*p'-n*-Alkoxycinnamoyloxy)benzylidene *p"-N,N*-diethylamino anilines.

n-Alkyl group	Transition temperatures °C		
	Smectic	Nematic	Isotropic
Methyl	—	181.0	211.0
Ethyl	—	150.0	218.0
Propyl	—	161.0	200.0
Butyl	—	148.5	200.5
Pentyl	—	144.0	187.5
Hexyl	—	138.0	185.0
Heptyl	—	115.0	176.5
Octyl	—	120.0	175.0
Decyl	—	119.0	168.0
Dodecyl	(100.0)	115.0	160.5
Hexadecyl	(112.0)	117.0	148.0
Octadecyl	(112.5)	113.0	142.0

Values in parenthesis indicate monotropy

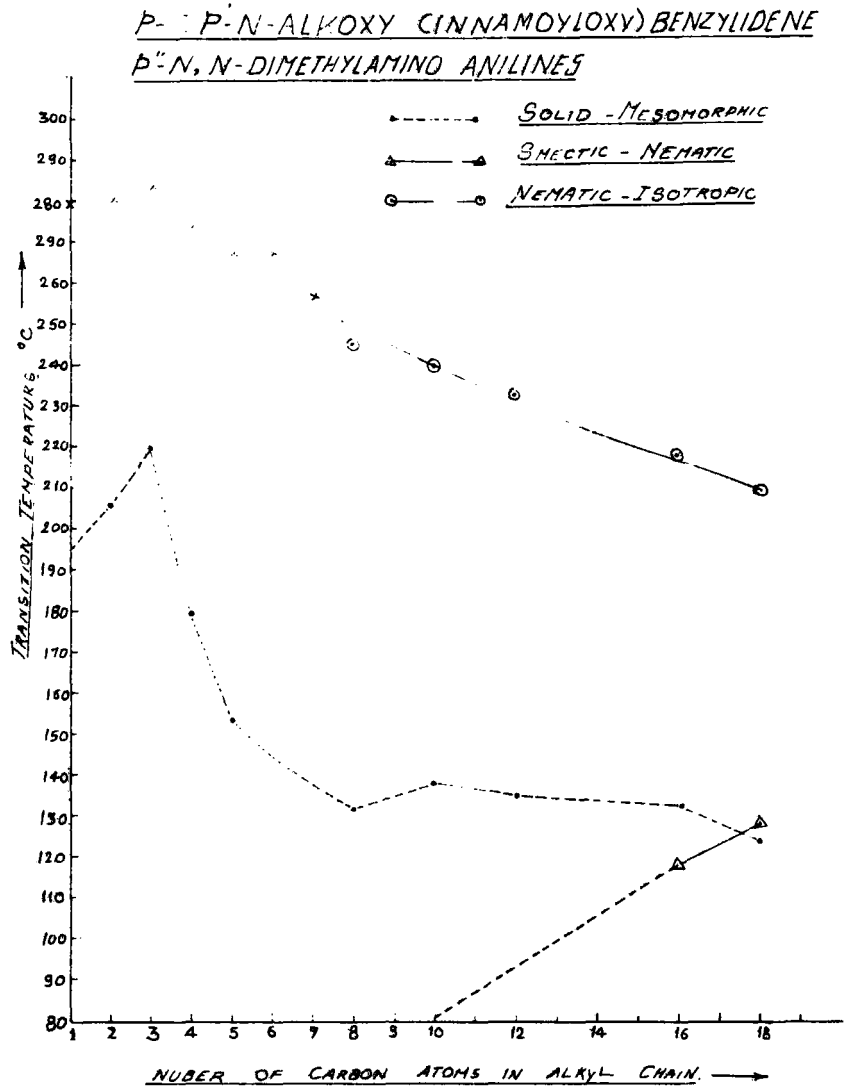


FIGURE 1

shows a steep rise upto the third homologue and then a steeper fall upto the eighth homologue. Thereafter the curve shows a little rise at the tenth homologue followed by a fall at the twelfth derivative. From the twelfth derivative to the sixteenth derivative the curve seems to level off and indicates a small fall of about 4° at the octadecyl derivative.

Only nematic mesophase is exhibited upto the octadecyl derivative of the homologous series on heating. Exhibition of polymesomorphism commences

in monotropic condition at the hexadecyl homologue and shows an enantiotropic smectic mesophase of about 2° range at the octadecyl member. The series has an overall nematogenic character which is a striking feature. The mesomorphic range is quite wide and varying, it being maximum, say 113° C, at the eighth member. The first seven members of the series decompose abruptly before they could reach their normal nematic-isotropic transitions—a smooth transition being ruled out on account of high thermal vibrations. The nematic-isotropic transition curve shows a steep descending tendency as the series is ascended. This is a characteristic feature of high melting series.

While some characteristics are similar, the homologous series (II): *p*-(*p'*-*n*-alkoxycinnamoyloxy) *p''*-*N*,*N*-diethylamino anilines differs in certain respects when compared with the series (I): viz. *p*-(*p'*-*n*-alkoxycinnamoyloxy)-benzylidene *p''*-*N*,*N*-diethylamino anilines.

Like series (I), the series (II) is also a high melting one, but the transitions are somewhat lower than those of series (I). The solid-mesomorphic (Figure 2) curve shows initially a steep fall from first to second member followed by a small rise at the third homologue. Thereafter there is an overall fall upto the seventh member with breaks through fourth, fifth and sixth members. It rises a little bit at the eighth homologue and then shows a negligible fall with a tendency to level off at the hexadecyl homologue followed by another negligible descending tendency as the octadecyl homologue is reached.

The nematic-isotropic transition curves show steep descending tendency as the series is ascended in keeping with the characteristics of high melting series. Unlike the dimethylamino aniline series (I), this series does not decompose at the initial level, hence odd-even effect in nematic-isotropic transition curves is very easily marked. The enantiotropic nematic phase is observed from the very first member.

Enantiotropic polymesomorphism is not exhibited by the homologous series *p*-(*p'*-*n*-alkoxycinnamoyloxy)benzylidene *p''*-*N*,*N*-diethylamino anilines, though smectic property in monotropic condition makes its appearance at the dodecyl derivative. The monotropic smectic-nematic transition curve rises smoothly showing slight curve as the series is ascended. Very careful supercooling of the anisotropic melts does not succeed in getting monotropic smectic phase below the twelfth homologues obviously because of high crystallizing tendency of the supercooled melts. Since lateral attractions are stronger in the series (II) as compared to those of dimethylamino aniline series (I), relatively early commencement of smectic property curve is quite natural. The extrapolation of the smectic-nematic monotropic transition curve to the left hand side indicates probable monotropic smectic phase transitions at 94° C, 89° C and 82° C for decyl, nonyl and octyl homologues respectively. The mesomorphic range is much narrower as compared to series (I).

The nature of the nematic phase is threaded while that of the smectic meso-

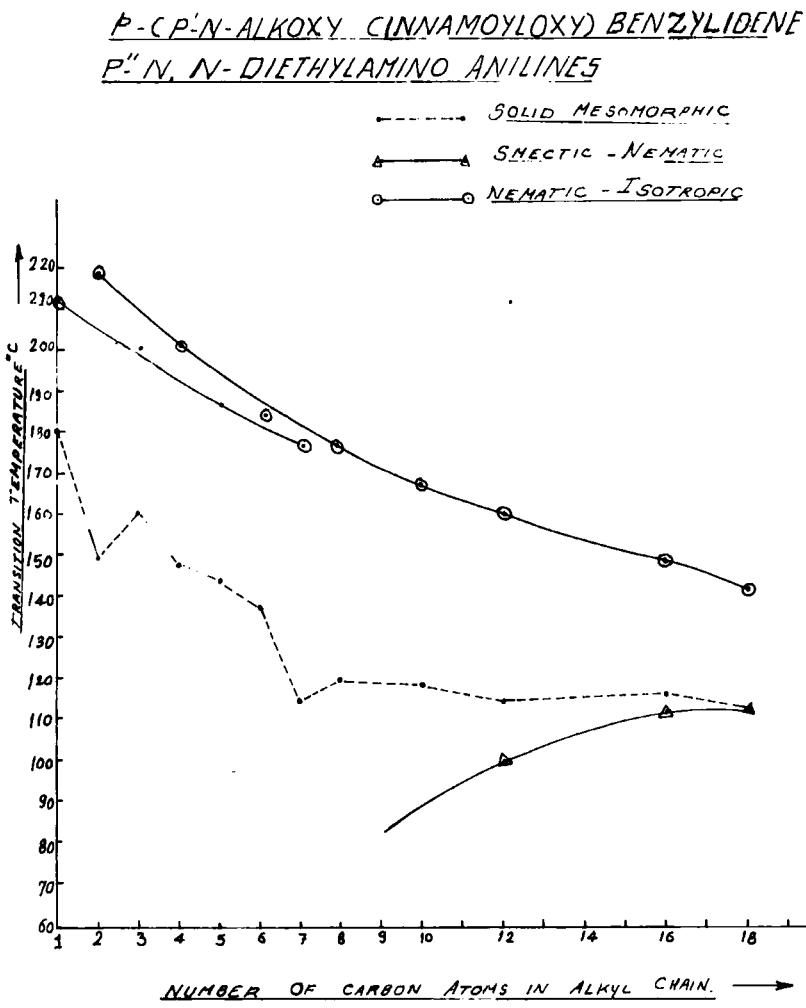


FIGURE 2

phase is of focal conic fan shaped belonging to smectic A variety in case of both homologous series.

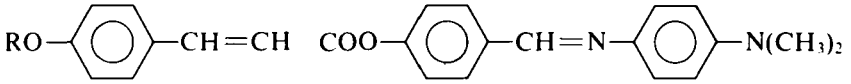
A general comparison of mesomorphic characteristics of series (I) and (II) mutually and with some other structurally related series[4-6] can be fruitful. Their molecular geometries are given in Figure 3. In Table III are recorded the average thermal stabilities.

The homologous series (I) is thermally more stable than the homologous series (II). From Figure 3 it is clear that the homologous series (I) resembles the series (II) in all respects, and differs only in one thing i.e., the terminal

TABLE III

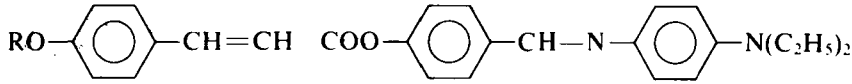
Average thermal stabilities

Series	I	II	A	B	C	D
Nematic-Isotropic	239.5 (C_8–C_{12})	167.8 (C_8–C_{12})	270.0 (C_6–C_8)	259.3 (C_8–C_{12})	252.6 (C_5–C_7)	227.6 (C_5–C_7)
Smectic-Nematic or Smectic-Isotropic	130.0 (C_{16}–C_{18})	115.0 (C_{16}–C_{18})	167.2 (C_{12}–C_{18})	182.7 (C_{16}–C_{18})	123.4 (C_{12}–C_{18})	154.2 (C_{12}–C_{18})
Commencement of Smectic mesophase	C_{16}	C_{12}	C_8	C_8	C_{12}	C_7



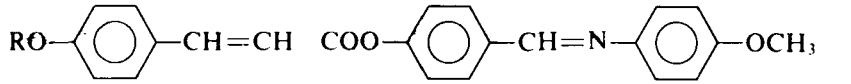
(I)

p-(*p'*-*n*-alkoxy cinnamoyloxy)benzylidene *p''*-*N*,*N*-dimethylamino anilines



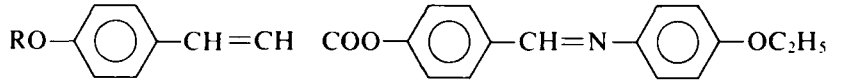
(II)

p-(*p'*-*n*-alkoxy cinnamoyloxy)benzylidene *p''*-*N*,*N*-diethylamino anilines



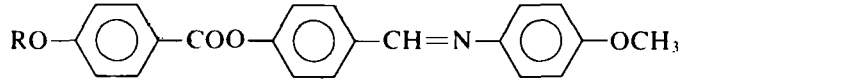
(A)[5]

p-(*p'*-*n*-alkoxy cinnamoyloxy)benzylidene *p''*-anisidines



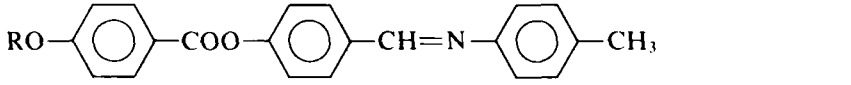
(B)[6]

p-(*p'*-*n*-alkoxy cinnamoyloxy)benzylidene *p''*-phenetidines



(C)[4]

p-(*p'*-*n*-alkoxy benzoyloxy)benzylidene *p''*-anisidines



(D)[4]

p-(*p'*-*n*-alkoxy benzoyloxy)benzylidene *p''*-toluidines

FIGURE 3 Homologous series under comparison.

group at the other end. In series (I) the group is $-N(CH_3)_2$, whereas in series (II) it is $-N(C_2H_5)_2$ group. The decreasing thermal stability in passing from $-N(CH_3)_2$ group (series I) to $-N(C_2H_5)_2$ group (series II) can be attributed to the alkyl chain getting prolonged beyond limit whereby the length to breadth ratio would be crossing the ideal optimum causing weakening of the molecular forces of adhesions which result into lower transitions.

An isomeric Schiffs base viz. *p*-dimethylamino benzal *p*-anisidine[11] is reported to be a non-mesomorphic compound. However, a third benzene ring and an added vinyl carboxy, —CH=CH—COO—, group add to the overall length of the molecules and enhance lateral attractions as well as polarizability. The $-NMe_2$, dimethylamino terminal group is mildly polar as compared to the alkoxy group, yet lengthwise its contribution could be better. The molecules will be sufficiently non-coplanar as well due to the bumping of the oxygen and hydrogen atoms of vinyl carboxy and azomethine central groups respectively into the non-bonded sides of the adjacent hydrogen atoms of the aromatic ring leading to a little bit lowering of transitions. While it is so the π electron density of the central bridges will be contributing towards stronger lateral attractions. The combined effect of all these factors is the one of very high transitions and thermal stability. Had the molecules not suffered a twist around C—O and C—H bonds they would have been quite coplanar, in which case, all other factors remaining as they are, the transitions would have been still higher leading to higher thermal stabilities than what these are.

It is interesting to note that the difference between the smectic-nematic or smectic-isotropic thermal stabilities between the series (I) and (II) is about 15.2° C while the difference in nematic-isotropic thermal stability for these series is about 71.7°C, approximately 4.7 times that of the smectic-nematic or smectic-isotropic thermal stability. While the molecular forces responsible for maintaining ordered arrangement in fluid condition seems to be working alright at lower temperatures, their capacity to resist vigorous thermal agitations falls off as the temperature is raised much higher, yielding a wider difference in the decreasing or falling nematic-isotropic thermal stability as the diethyl unit is substituted in place of dimethyl.

When the smectic-nematic or smectic-isotropic thermal stabilities of the homologues of the homologous series (I) and (II) are compared with those of the homologous series (A) and (B), the thing that strikes out remarkably is their unusually very high values as compared to series (I) and (II). All the homologous series (I), (II), (A) and (B) have almost the same molecular characteristics including (i) central bridges, viz. vinyl carboxy, —CH=CH—COO— and —CH=N—, azomethine, (ii) three benzene rings and (iii) alkoxy groups at one end, excepting the other terminal groups viz. $-NMe_2$, $-NEt_2$, $-OCH_3$, $-OC_2H_5$ for series (I), (II), (A) and (B) respectively. It can be observed that —OMe and —OEt groups are highly polar groups; hence the high

polarity of —OMe and —OEt groups in case of series (A) and (B) cause smectic-nematic or smectic-isotropic thermal stability to be greatly enhanced. The nematic-isotropic thermal stability of the series (A) and (B) homologues is also greatly enhanced for the same reason.

On comparing the smectic-nematic or smectic-isotropic thermal stabilities of the homologous series (I) and (II) with those of the series (C) and (D), certain striking points emerge. The homologous series (C) and (D) have carboxy, —COO—, central bridge as one of the two central bridges while series (I) and (II) have vinyl carboxy, —CH=CH—COO—, at the corresponding place. The resultant non-coplanarity due to a twist received on account of the bumping of the oxygen and hydrogen atoms into the non-bonded hydrogen atoms of the adjacent benzene rings will almost be the same, though the lateral forces due to —CH=CH—COO—, bridge in series (I) and (II) will be more on account of enhanced length and the added double bond. If the smectic-nematic or smectic-isotropic thermal stability of the series (D) is more than that of series (I) and (II), it is because of the fact that smectic thermal stability for the series (C) and (D) will be following an alternating pattern. Also if the smectic thermal stability of the series (II) homologues is less than that of the series (C) homologues, it is because of the decreasing tendency of the series (I) and (II) homologues as discussed in terms of the 'dimethyl' and 'diethyl' units. Now $-OCH_3$ group in case of the series (C) homologues endows the molecules with high polarity which enhances the smectic-nematic thermal stability to some extent as compared to series (II). In the same manner, the $-NMe_2$ and $-NEt_2$ groups at the other terminal in case of the series (I) and (II), being not sufficiently polar, work towards lowering of the transitions. These three aspects in a combined manner yield the smectic thermal stability values as they are.

The nematic-isotropic thermal stability values of the series (C) is higher than those of the series (I) and (II). It is the polar nature of the $-OCH_3$ terminal group of the series (C) that increases the polarity and polarizability of the molecules resulting into higher thermal stability. If the nematic-isotropic thermal stability of series (D) homologues, where the other terminal group is $-CH_3$ which is comparable polarity wise with NMe_2 and NEt_2 is higher than that of the series (II) homologues, it is because of the alternating characteristics of the series (C) and (D) and decreasing characteristics of the series (I) and (II), the two characteristics being incompatible.

Very late commencement of the smectic mesophase in case of series (I) and (II) may be due to weakening of the lateral attractions because of the disproportionate length to breadth ratio in these homologues. Comparatively the smectic mesophase commences quite early in case of series (A), (B) and (D) either because lateral to terminal attractions maintain the proportionate molecular force or the lateral attractions predominate over the terminal attractions.

In the case of the series (I) and (II), the number of methylene units remains

'even' when a 'dimethyl' unit is replaced by 'diethyl' unit. Obviously, the total number of units remaining even, the alternating effect of transition may be ruled out. The decreasing transitions of the homologues of the homologous series (II) as compared to those of the series (I) may be viewed in this light and another homologous series as and when synthesized with the characteristics of series (I) and (II) but with 'dipropyl' group at the other terminal may be predicted to have lesser transitions.

Gray[12] has reported two compounds viz. *p*-ethoxy benzylidene *p'*-*N*,*N*-dimethylamino aniline and *p*-ethoxy benzylidene *p'*-*N*,*N*-dimethylamino biphenyl aniline with K–I = 140°(102°) and K–N = 208°, N–I = 274° transitions respectively. When these transitions are compared with the transitions of the *p*-(*p'*-ethoxycinnamoyloxy)benzylidene *p''*-*N*,*N*-dimethylamino aniline, it gives an interesting observation. There are a good many common molecular characteristics. One terminal ethoxy group, two benzene rings and an azomethine central group as well as —NMe_2 as another terminal group, are the common features. In case of the biphenyl compound, it has a third benzene ring in common with the '*p*–*p*' ethoxy compound of the series (I). It can be seen that with an added longer vinyl carboxy, —CH=CH—COO—, central bridge, the transitions of the *p*-(*p'*-ethoxycinnamoyloxy)benzylidene *p''*-*N*,*N*-dimethylamino aniline with K–I = 206° and N–I = 295° (d), are quite high as compared to the transitions of the compounds under comparison—obviously a contribution of the enhanced polarizability.

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