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Mesomorphic Characteristics and Phase Transitions of Some New Mesogens I: *p*-(*p*′-*n*-Alkoxycinnamoyloxy)benzal *p*″-phenetidines

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Twelve new mesomorphs belonging to the homologous series of mesogens: *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzal *p*″-phenetidines have been synthesized. This is a high melting homologous series of mesomorphs. The first four members decompose at very high temperatures; the pentyl, hexyl and heptyl derivatives exhibit enantiotropic nematic threaded texture. Polymesomorphism commences from the eighth member and continues up to the last viz. octadecyl derivative. The smectic phase shows focal conic fan shaped texture of the smectic A variety. The usual odd–even effect is observed in the case of nematic–isotropic transitions. The smectic–nematic transition curve rises steeply as the series is ascended increasing the smectic range at the cost of the nematic mesophase. The mesomorphic phases offer wide ranges and the thermal stabilities are as per the molecular geometry and the substituents responsible for the overall molecular forces.

INTRODUCTION

A good number of mesogens belong to homologous series of Schiffs bases, acids and esters. Quite a few homologous series comprising both ester linkage and azomethine group in the middle[1-4] have been studied. Some of these Schiffs base esters are purely smectogenic, while others are both smectogenic and nematogenic. The present new homologous series has been synthesized with the view to explore the mesomorphic behaviour and its temperature dependence due to change in the *p*-substituent and central linkage.

EXPERIMENTAL

Synthesis

1. *p-n-Alkoxybenzaldehydes:* These were prepared by the method of Vyas and Shah.[5]

2. *Trans-p-n-alkoxycinnamic acids:* These were prepared from the corresponding *p-n*-alkoxybenzaldehydes and malonic acid.[6]

3. *Trans-p-n-alkoxycinnamoyl chlorides:* These were prepared from the corresponding trans-*p-n*-alkoxycinnamic acids.[7]

4. *Preparation of esters: p-(p′-n-Alkoxycinnamoyloxy)benzaldehydes:* These were prepared by reacting trans-*p-n*-alkoxycinnamoyl chlorides with *p*-hydroxybenzaldehyde.[8]

5. *Preparation of Schiffs bases: p-(p′-n-Alkoxycinnamoyloxy)benzal p″-phenetidines:* These were prepared by condensing *p*-(*p′-n*-alkoxycinnamoyloxy)benzaldehydes with *p*-phenetidine. Equimolar amounts (0.01 mole) of *p*-(*p′-n*-alkoxycinnamoyloxy)benzaldehyde and *p*-phenetidine are refluxed for one hour in 20–25 ml ethanol containing a few drops of acetic acid. The products were crystallized from benzene : alcohol (20 : 80) mixture. The melting points and transitions are given in Table I.

TABLE I

p-(*p′-n*-Alkoxycinnamoyloxy)benzal *p″*-phenetidines

	Transition temperatures (°C)			
n-Alkyl group	Smectic	Nematic	Isotropic	
1 Methyl	—	145.0	310.0[d]	333.0[a]
2 Ethyl	—	165.0	301.0[d]	333.0[a]
3 Propyl	—	148.0	302.0[d]	315.0[a]
4 Butyl	—	150.0	300.0[d]	312.0[a]
5 Pentyl	—	137.0	297.0	
6 Hexyl	—	126.0	293.0	
7 Heptyl	—	112.0	278.5	
8 Octyl	109.0	125.0	273.0	
9 Decyl	112.0	153.0	261.0	
10 Dodecyl	112.0	170.5	244.0	
11 Hexadecyl	112.0	179.5	214.0	
12 Octadecyl	113.0	186.0	204.0	

[a] Values obtained by extrapolation.

[d] Decomposition point. The elemental analysis conforms with the calculated values.

STUDY

The transitions were studied by the usual optical method as well as by using Kofler heating stage polarizing microscope.

RESULTS AND DISCUSSION

The new homologous series is a very high melting series with wide mesomorphic range and high thermal stability.

The plot of solid–mesomorphic transitions versus the number of carbon atoms in the alkyl chain of the alkoxy end shows an alternation of rise and fall followed by a steep fall and ending with levels off with negligible variations.

Enantiotropic nematic mesophase is exhibited up to the seventh member. Polymesomorphism begins from the eighth member and persists up to the octadecyl homologue (Figure 1). The first four members exhibit mesomorphic range of about 150 °C; they, however, decompose before reaching mesomorphic–isotropic transitions. The molecules cannot resist high thermal vibrations at such high temperature and break down all of a sudden eliminating smooth transition to isotropic liquid.

The nematic–isotropic transition curves show the usual odd-even effect though the two curves are very near each other. These curves show a steep fall as the series is ascended obviously as the series is a high melting one. The two nematic–isotropic transition curves are extrapolated to the left side indicating the temperatures 333 °C, 333 °C, 315 °C and 312 °C as nematic–isotropic transitions for the methyl, ethyl, propyl and butyl derivatives, respectively.

Since the terminal attractions due to polar ends are high enough as compared to the lateral forces, nematic mesophase is exhibited up to the heptyl homologue. Both smectic and nematic mesophases are exhibited from the eighth homologue onwards, since the increased chain length of the alkyl group affects considerably the ratio of lateral to terminal attractions so as to allow strata formation to take place. The nematic mesophase persists from 125 °C to 273 °C; this is a very wide range indeed. The nematic–isotropic transition curve from the octyl member does not follow alternation but shows a steep but smooth fall up to the octadecyl member of the homologous series. The smectic–nematic transition curve from the octyl derivative onwards, on the other hand, shows first a steep rise up to the dodecyl derivative followed by a smooth rise as the series is ascended up to the octadecyl

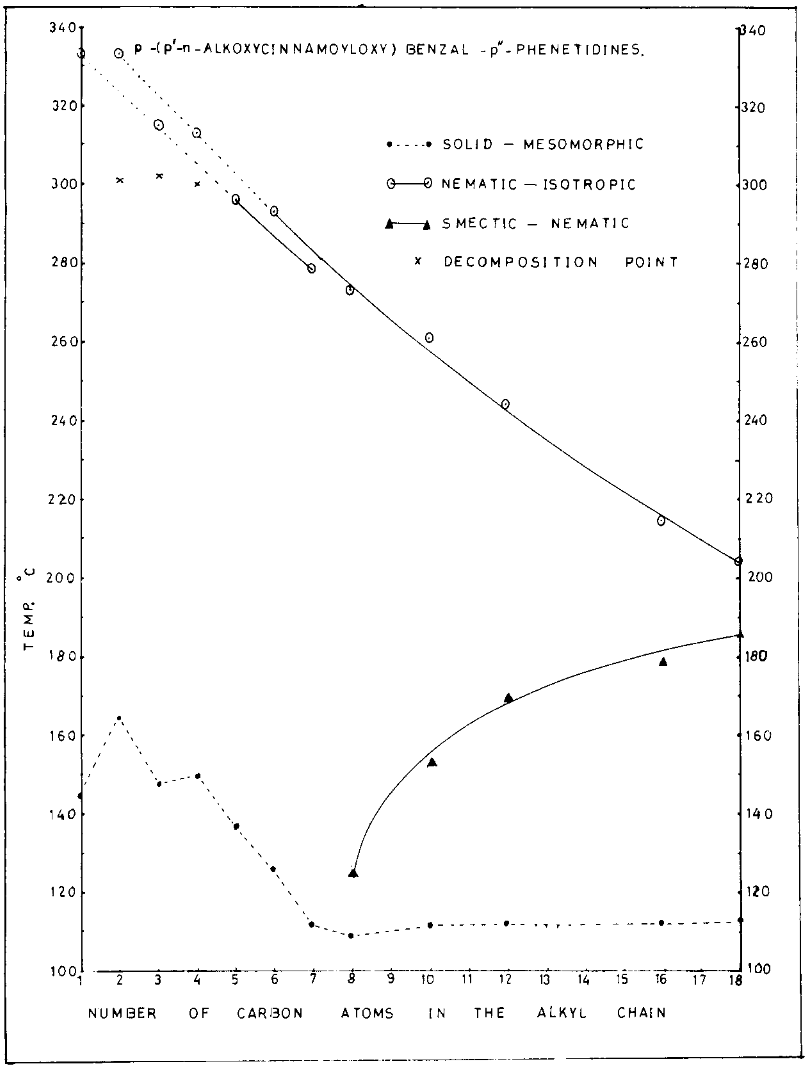

FIGURE 1

homologue. On account of the falling nature of one transition curve and rising nature of the other, the nematic mesophase narrows down while the smectic mesophase widens up from the octyl to octadecyl homologues of the homologous series. Polymesomorphism persists up to the eighteenth member. Pure smectic phase is absent in the case of this series. The nematic mesophase range of about 148 °C at the octyl homologue gets reduced to about 17 °C at the octadecyl level while the range of smectic mesophase increases from about 16 °C at the eighth member to about 73 °C at the octadecyl derivative. Enhanced polarizability due to the lengthening of the alkyl chain as the series is ascended in addition to the lateral attractions emanating from the π electrons of the two central bridges are the reasons for enhanced smectic mesophase in the polymesomorphic region. Judging from the falling and rising nature of the two transition curves, the nematic mesophase is more likely to disappear at the twenty-first member.

Due to the extremely steep nature of the smectic–nematic curve any possibility of finding out latent smectic–nematic transition temperatures for the seventh and sixth members is ruled out.

The texture of the nematic mesophase is a threaded one. The stratified smectic mesophase assumes focal conic fan-shaped structure of smectic A type. The transitions from one to the other phase are quite sharp both on heating and on cooling.

Thermal stabilities of the *p*-(*p*′-*n*-alkoxycinnamoyloxy)benzal *p*″-phenetidines are compared with those of certain other series whose molecular geometry is parallel. All the homologous series have three aromatic rings and two central bridges excepting the series G and comparable terminal groups. The present homologous series can be obtained by extending the corresponding molecules of the series G by reacting with *p*-phenetidine. Both central bridges viz. vinyl carboxy, —CH=CH · COO—, and azomethine, —CH=N—, endow the molecules with non-coplanarity. The extent of non-coplanarity will thus be the same for homologues of all the above series excepting those of the series G which is having only one central bridge and two benzene rings.

The lowest nematic–isotropic thermal stability is for the series G since the overall terminal and lateral attractions are comparatively less in the case of its molecules. The present series has the highest nematic-isotropic thermal stability. The molecules of the present series have a highly polar end group, $—OC_2H_5$ at the right terminal as compared to the corresponding terminal groups $—CH_3$ or $—OCH_3$ of the other series. All other aspects are the same.

It is the high polarity of the $—OC_2H_5$ terminal group and proportionate increase in the length of the group due to addition of an alkyl unit that their nematic–isotropic thermal stability is the highest. The series N, K_1 and K_2 have the same molecular geometry but their terminal groups at the right end differ in polarity. The series N has more nematic–isotropic thermal stability than those for series K_1 and K_2 because of its least ratio of lateral to terminal attractions among the three series under comparison.

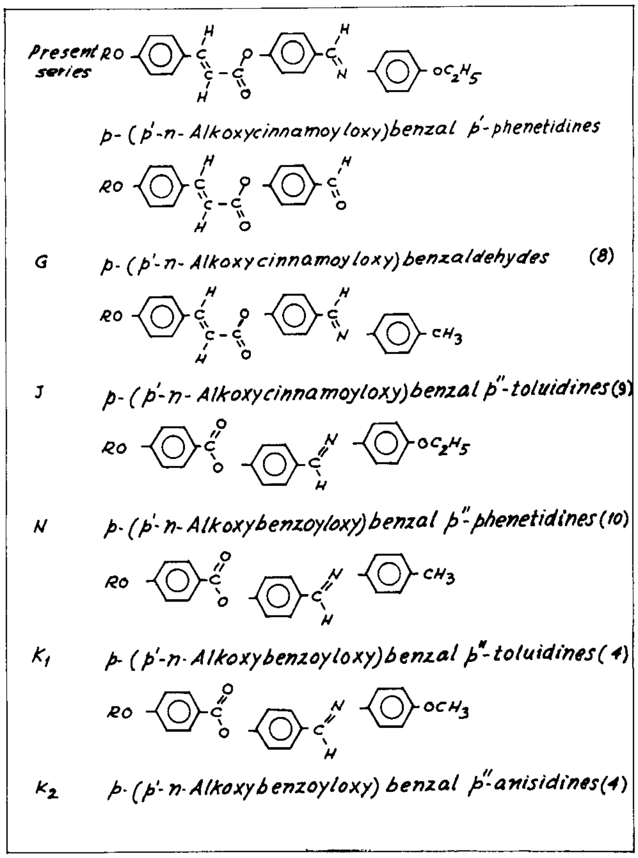

FIGURE 2

TABLE II

Average Thermal Stabilities in °C

Series	Present series	G	J	N	K_1	K_2
Nematic–Isotropic (C_5–C_7)	289.5	111.0	255.8	258.6	227.6	252.6
Smectic–Nematic or Smectic–Isotropic (C_{12}–C_{18})	178.6	118.0	190.0	149.5	154.2	123.4
Commencement of Smectic mesophase	C_8	C_8	C_7	C_{10}	C_7	C_{12}

Both N and the present series have almost similar structural geometry. However, one of the central bridges is different in series N—it being a shorter carboxy in place of a slightly longer vinyl carboxy. With this difference, the enantiotropic nematic mesophase in the case of N series commences from the very first member and continues up to nonyl derivative. But in the case of the present series though the nematic mesophase commences from the very first member and continues up to heptyl derivative, the first four members decompose at higher temperatures since the longer central bridge —CH=CH · COO— scale up the transitions due to increased polarizability.

Some of the striking features of the present series are (i) decomposition of the first four members, (ii) high smectic and nematic thermal stabilities and (iii) early commencement of the smectic phase due to introduction of the vinylcarboxy, —CH=CH · COO-group. The central bridge —CH=CH · COO— increases the ratio of lateral to terminal attractions as well as the overall polarizability which enhance the smectic as well as nematic thermal stabilities. Moreover it also plays an important role in the early commencement of the smectic mesophase.

The nematic–isotropic thermal stability of the present series is higher than that of the series J due to the high polarity of the —OC_2H_5 group.

However the case of the smectic–isotropic or smectic–nematic thermal stabilities for the homologues of the above homologous series is somewhat different. Since the ratio of lateral to terminal attractions in the case of series J is higher than that for the present series, the smectic-nematic thermal stability for the molecules of the series J should be higher, and it is so. In the case of the molecules of series K_1 and K_2, lower smectic–nematic or smectic–isotropic thermal stabilities are due to the shorter middle carboxy group causing lesser overall polarizability of the molecules as compared to the molecules of the present series. However, the homologues of series K_1 which have a less polar terminal group —CH_3 at the other end, are having higher smectic–nematic thermal stability than that of the series K_2 molecules as the ratio of lateral to terminal attractions in the case of series K_1 homologues is higher. Obviously, with absence of one benzene ring and one central bridge as compared to the other series, the smectic–nematic thermal stability for the homologues of the series G is the lowest as their overall polarizability is also the lowest among the six series taken for comparison.

Commencement of the smectic mesophase in the present homologous series is at the octyl homologue and in series G, J and K_1 at the heptyl homologues. This speaks for their strong lateral attractions. With relatively greater terminal attractions in the case of series N and K_2 homologues due to highly polar $-OC_2H_5$ and $-OCH_3$ groups at the other end respectively, the smectic mesophase commences so late as from decyl and dodecyl stages respectively when suitable ratio of lateral to terminal attractions is achieved with the proper chain length of decyloxy and dodecyloxy and higher groups conducive to emergence of smectic mesophase.

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