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Mesomorphic Characteristics of Liquid Crystalline Esters *p*-Methoxyphenyl *p*-Alkoxycinnamates

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The newly synthesized homologous series *p*-methoxyphenyl *p*-alkoxycinnamates **(I)** can be compared with the series *N*-[*p*-(*p*-alkoxycinnamoyloxy)benzylidene] *p*-anisidines **(II)**.1) All the homologues of both the series **(I)** and **(II)** from C_1 to C_{18} are mesogens. In series **(II)** the first five members decompose due to high transitions at about 300 °C. With decrease in length of the molecules of series **(I)** than that of series **(II)**, the overall transitions also decrease by about 150 °C. The first seven members in series **(II)** are nematogens; polymesomorphism begins from octyloxy homologue with the commencement of smectic mesophase and continues to be exhibited upto the last i.e. octadecyloxy homologue. In series **(I)** also the nematic phase is exhibited upto the heptyl derivative; the smectic phase commences from C_8-member in the form of monotropic phase thereby exhibiting polymesomorphism upto the C_{14} homologue. The last two members of series **(II)** are smectogens. The odd-even effect is missing in series **(II)** whereas in series **(I)**, it is seen upto the fifth homologue. In both the series, the N-I curves show a falling tendency— a criterion of high melting series. From textures' point of view both the series have common features, the nematic phase is threaded when it is the only mesophase shown and homeotropic in polymesomorphic region, whereas the smectic mesophase is focal conic fan shaped of smectic-A variety. This series also yields interesting comparison with the series (III) *p*-nitrophenyl *p*-alkoxycinnamates4) and (IV) *p*-chlorophenyl *p*-alkoxycinnamates.5)

The mesomorphism exhibited by a number of homologous series can be attributed to their molecular geometry and the effect of the molecular forces due to them. Earlier studies1—3,15) of homologous series with ester and azomethine linkages have been reported. Further, the series with ester linkage as a central bridge and NO_2 and Cl as terminal groups4,5) have also been reported. A number of homologous series with alkoxy as terminal substituent has been reported in literature.6—8) We report here a homologous series of ester mesogens with $-CH{=}CH-COO-$ as the central bridge and $-OCH_3$ as the terminal group viz. *p*-methoxyphenyl *p*-alkoxycinnamates. The mesomorphic characteristics and the variations in liquid crystalline properties of this series are compared with the earlier reported series viz. *N*-[*p*-(*p*-alkoxycinnamoyloxy)benzylidene]-*p*-anisidines.1)

Experimental

Preparation: (i) *p*-Alkoxy benzaldehydes, (ii) *trans-p*-alkoxycinnamic acids, and (iii) *trans-p*-alkoxycinnamoyl chlorides were prepared by the reported methods.9—11)

(iv) *p*-methoxyphenyl *p*-alkoxycinnamates: These esters were synthesized by refluxing the mixture of *trans-p*-alkoxycinnamoyl chlorides (0.015 mol) with *p*-methoxyphenol (0.01 mol) in dry pyridine (10.0 ml) for 2 h and then allowed to stand overnight. After distilling the excess $SOCl_2$, it was acidified with dilute HCl and the resulting precipitated products were washed with water and NaOH and purified with column chromatography and then recrystallized from ethanol or ethyl acetate–ethanol (10 : 90) mixture. The C, H, N elemental analysis data for the homologues obtained from Coleman U.S.A. (model 33) confirm with the calculated ones. (Table 1).

Table 1. *p*-Methoxyphenyl *p*-Alkoxycinnamates

n-Alkyl group	Molecular formula	Required/%		Found/%	
		C	H	C	H
Methyl	$C_{17}H_{16}O_4$	71.830	5.663	71.69	5.703
Ethyl	$C_{18}H_{18}O_4$	72.483	6.040	72.00	6.008
Propyl	$C_{19}H_{20}O_4$	73.076	6.410	72.60	6.645
Butyl	$C_{20}H_{22}O_4$	73.619	6.748	73.30	7.205
Pentyl	$C_{21}H_{24}O_4$	74.117	7.058	73.95	7.164
Hexyl	$C_{22}H_{26}O_4$	74.576	7.344	74.15	7.543
Heptyl	$C_{23}H_{28}O_4$	75.000	7.604	74.57	7.932
Octyl	$C_{24}H_{30}O_4$	75.392	7.853	74.98	7.707
Decyl	$C_{26}H_{34}O_4$	76.097	8.292	75.68	8.604
Dodecyl	$C_{28}H_{38}O_4$	76.712	8.675	76.58	8.622
Tetradecyl	$C_{30}H_{42}O_4$	77.253	9.012	77.32	9.049
Hexadecyl	$C_{32}H_{46}O_4$	77.732	9.311	77.39	8.976
Octadecyl	$C_{34}H_{50}O_4$	78.160	9.578	77.80	10.000

Method of Study: The transitions and other characteristics were studied using Kofler heating stage polarizing microscope.

Results and Discussion

All the homologues of series **(I)** *p*-methoxyphenyl *p*-alkoxycinnamates from C_1 to C_8 are mesogens (Fig. 1) and are high melting ones since the N-I and S-I curves show falling12) tendency. The K-M curve shows the overall falling tendency upto the last member. Both the N-I curves show the alternation effect upto the fifth member; after which the curve steadily falls as the series is ascended ending abruptly at the C_{14} homologue. Polymesomorphism begins from the C_8 member in monotropic conditions with the advent of S_A phase and persists upto the C_{14} homologoue; the last two members

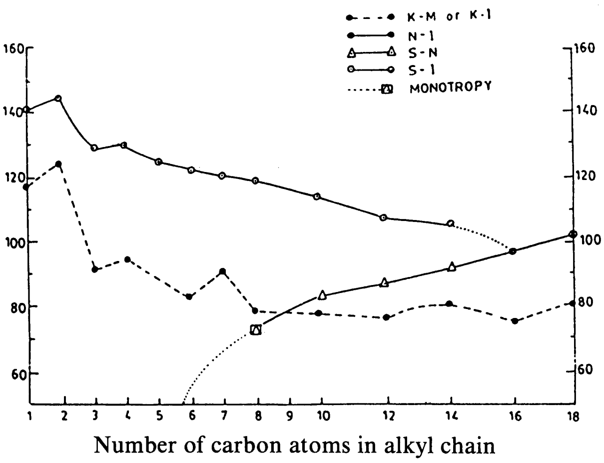


Fig. 1. *p*-Methoxyphenyl *p*-alkoxycinnamates.

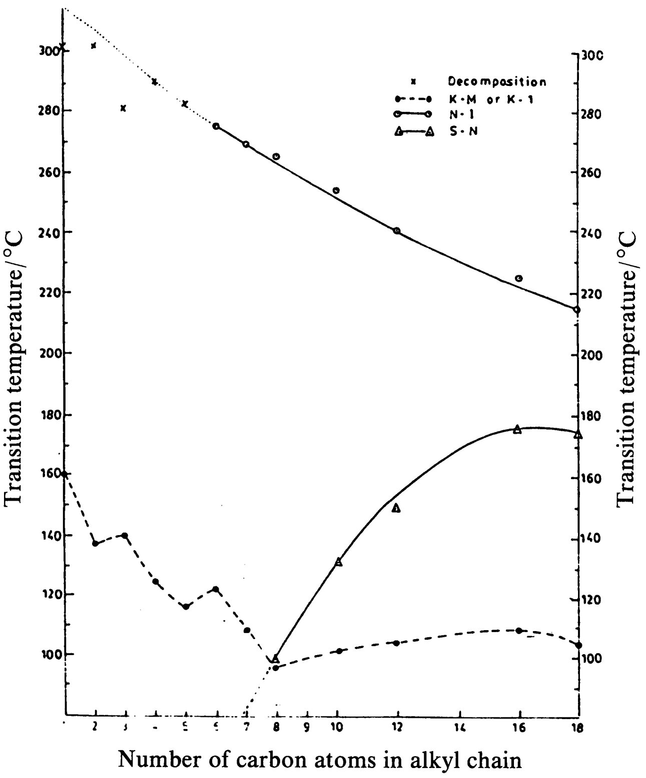


Fig. 2. *N*-[*p*-(*p*-Alkoxycinnamoyloxy)benzylidene]-*p*-anisidines.

are purely smectogens. The S-N curve rises gradually with the ascending of the series and seems to be merging with the falling S-I curve. Though a majority of the homologues are either polymesomorphic or purely smectogens, the smectic phase length is never bigger than the nematic phase length; even overal mesomorphic range is between 35 to 40 °C. Alternately, the falling tendency of the N-I curve is well-matched by the rising tendency of the S-N curve and hence the smectic phase length does not increase at the cost of nematic phase in the polymesomorphic region. Intrapolation of the S-N curve indicates the LTT values for the C_7 and C_6 members at 65.5 and 55° respectively. The texture of the nematic phase is threaded; where it is the only mesophase shown, however, it is homeotropic in the polymesomorphic region, whereas the smectic phase shows focal conic fan shaped texture of S_A variety.

The series (**I**) offers interesting comparison with the series (**II**) viz. *N*-[*p*-(*p*-alkoxycinnamoyloxy)-benzylidene]-*p*-anisidines.[1] All the homologoues of series (**II**) are also mesogens (Fig. 2) like those of series (**I**). The series (**II**) with one more benzene ring and -CH=N-linkage show high transitions as compared to series (**I**); even the first five members of the series (**II**) decompose at about 300 °C. With decrease in length of series (**I**) the overall transitions also fall by about 160 °C. The series (**II**) shows polymesomorphism beyond C_7 homologoue and continues to be exhibited upto the last. However, in series (**I**) the polymesomorphism is exhibited between C_8 (monotropic) and C_{14} homologoue. The odd-even effect is absent in series (**II**) whereas series (**I**) shows alternation in N-I curves upto the 5th member. The K-M curve in series (**II**) shows overall falling tendency which contributes towards increase in mesomorphic range of about 150 to 160 °C in an overall manner, whereas in series (**I**) the mesomorphic range is between 35 to 40 °C. The textures of series (**II**) are similar to those of series (**I**).

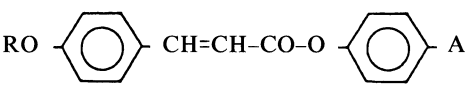
The series (**I**) also exhibits interesting comparison with the series (**III**) viz. *p*-nitrophenyl *p*-alkoxycinnamates[4] and series (**IV**) viz. *p*-chlorophenyl *p*-alkoxycinnamates.[5] Most of the molecular geometry of these series is common, the only uncommon part being the different terminal group at one end, $-NO_2$ in series (**III**) and -Cl in series (**IV**). In series (**III**) and (**IV**) the first two members are nonmesogens. Polymesomorphism is exhibited between C_6 and C_7 member in series (**III**) whereas it is exhibited between C_4 and C_6 members in series (**IV**). Series (**III**) shows high transitions as compared to series (**I**) whereas series (**IV**) shows almost comparable transitions with series (**I**).

Table 2 shows the average thermal stabilities and the stage of commencement of the smectic phase for the following homologous series selected for comparative study: *p*-Methoxyphenyl *p*-alkoxycinnamates (**I**); *p*-Nitrophenyl *p*-alkoxycinnamates[4] (**III**); *p*-Chlorophenyl *p*-alkoxycinnamates[5] (**IV**); *p*-(*p*-Alkoxycinnamoyloxy)acetophenones[13] (**V**); Methyl *p*-(*p*-alkoxycinnamoyloxy)benzoates[14] (**VI**).

Table 2. Average Thermal Stability (°C) of Homologous Series

Series	N-I	S-N or S-I	Commencement of S_m phase
I	126 (C_4—C_6)	95-1 (C_{12}—C_{18})	C_8
III	121.2 (C_4—C_6)	136.0 (C_{12}—C_{18})	C_6
IV	121.2 (C_4—C_6)	114.5 (C_{12}—C_{18})	C_4
V	136.8 (C_4—C_6)	139.7 (C_{12}—C_{18})	C_5
VI	138.3 (C_4—C_6)	131.7 (C_{10}—C_{18})	C_4

The general structure of these series taken for comparative study can be given as.



where

A = -OCH_3, -NO_2, -Cl, -$COCH_3$, -$COOCH_3$ for series **(I)**, **(III)**, **(IV)**, **(V)**, **(VI)**.

Most of the molecular geometry of all the homologous series under comparison is common, the only uncommon part being the different terminal groups at one end in them. The reason for the variations observed in the average thermal stabilities and the commencement of the smectic phase can be looked upon due to the different terminal groups of these series and the molecular forces arising therefrom. The lower N-I thermal stabilities may be due to the less terminal attractions. The higher N-I stability may be due to the polar terminal -OCH_3 group of series **(I)** or longer -$COCH_3$, -$COOCH_3$ terminal groups of series **(V)** and **(VI)** respectively.18) The higher S-N or S-I thermal stabilities may be due to the overall polarizability of the molecules and higher lateral attractions of the molecules.16) Eventhough NO_2 group is polar, the N-I stability for the series **(III)** is not high; it should also be mentioned that series **(III)** has also higher S-N or S-I stability which in fact is somewhat in contravention to the normally accepted generalization regarding the NO_2 group.17)

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