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Effect of Lateral Substitution on Mesomorphism: (A) 4(4'-n-Alkoxybenzoyloxy)-3-methoxy benzaldehydes (B) 4(4'-n-Alkoxybenzoyloxy)-3-methoxy benzylidene-4''-toluidines (C) 4(4'-n-Alkoxybenzoyloxy)-3-methoxy benzylidene-4''-anisidines

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Effect of Lateral Substitution on Mesomorphism:

(A) 4(4'-*n*-Alkoxybenzoyloxy)-
3-methoxy benzaldehydes
(B) 4(4'-*n*-Alkoxybenzoyloxy)-
3-methoxy benzylidene-4''-toluidines
(C) 4(4'-*n*-Alkoxybenzoyloxy)-
3-methoxy benzylidene-4''-anisidines

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Three homologous series, having a lateral substituent and different end groups have been synthesized. Series (A) is non-mesogenic while series (B) and (C) exhibit only nematic mesophase. The thermal stabilities of series (B) and (C) are much more lowered compared with the corresponding unsubstituted homologous series. Generally the introduction of a lateral substituent renders the system low melting, and the mesomorphic-isotropic transition temperatures are also lowered. However, in the present study, introduction of a bulky methoxy group as a lateral substituent lowers the mesomorphic-isotropic transition temperatures to a great extent but the melting points are not much depressed.

INTRODUCTION

Recently due to the applications of ambient liquid crystals in different fields, the synthesis of low melting smectic, nematic and cholesteric liquid crystals with broad mesophase ranges is of great importance. Lateral substituents like chlorine or methyl were known to reduce the crystal-mesophase transition temperatures quite effectively.^{1,2} In light of this it seemed of interest to synthesize homologous series with a methoxy group as a lateral substituent which

may depress the crystal-mesomorphic transition temperatures giving low melting mesogens. Three homologous series with a lateral methoxy group were synthesized and their mesomorphic behavior was studied.

EXPERIMENTAL

i) 4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides were prepared as described by Dave and Vora.³

ii) 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes (A).

These were prepared by reacting the appropriate 4-*n*-alkoxybenzoyl chlorides (0.01 mole) with 4-hydroxy-3-methoxy benzaldehyde (Vanilin, 0.01 mole) in pyridine (10 ml) initially at about 10°C, then heated on water bath for 1 hour and allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid and the precipitate was washed with dilute sodium hydroxide solution, followed by water. The esters were crystallized from ethanol until constant melting points were obtained. The elemental analytical data were satisfactory.

iii) 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzyldine-4"-toluidines (B).

The aldehydes of series (A) were refluxed with equimolar quantities of *p*-toluidine in ethanol for about two to four hours. The Schiff bases obtained on cooling were crystallized several times from ethanol till constant transition temperatures were obtained. These are reported in Table I. The elemental analytical data were satisfactory.

iv) 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzyldene-4"-anisidines (C).⁴

These Schiff bases were synthesized as described above by taking *p*-anisidine in place of *p*-toluidine. The melting points and transition temperatures are reported in Table I. The elemental analytical data were satisfactory.

v) Determination of Transition Temperatures

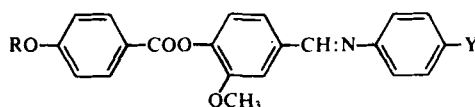
The optical observations were made by using a Mettler FP-2 polarizing microscope equipped with a heating device.

RESULTS AND DISCUSSION

Series A: 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzaldehydes.

All the members of this series are non-mesogenic. The corresponding homologous series without a lateral substituent exhibits mesomorphism.⁵ The non-mesogenic behavior of the present series can be attributed to the presence of a lateral bulky methoxy group which increases the breadth and steric hindrance. Even though the series is non-mesogenic, the melting points are not

TABLE I

R = C₁ - C₁₈ *n*-alkyl chain

Compound No.	R	Y	Transition Temperatures °C	
			N	I
<i>Series B</i>				
1	Methyl	Methyl	(163.0)*	181.0
2	Ethyl	Methyl	166.0	170.0
3	Propyl	Methyl	105.0	155.0
4	Butyl	Methyl	120.0	155.0
5	Pentyl	Methyl	121.0	131.0
6	Hexyl	Methyl	98.0	132.0
7	Heptyl	Methyl	97.0	123.0
8	Octyl	Methyl	97.0	122.0
9	Decyl	Methyl	94.0	113.0
10	Dodecyl	Methyl	88.0	104.0
11	Tetradecyl	Methyl	88.0	100.0
12	Hexadecyl	Methyl	90.0	94.0
13	Octadecyl	Methyl	(87.0)	90.0
<i>Series C</i>				
14	Methyl	Methoxy	192.0	207.0
15	Ethyl	Methoxy	149.0	214.0
16	Propyl	Methoxy	135.0	191.0
17	Butyl	Methoxy	131.0	184.0
18	Pentyl	Methoxy	121.0	175.0
19	Hexyl	Methoxy	115.0	161.0
20	Heptyl	Methoxy	107.0	153.0
21	Octyl	Methoxy	113.0	144.0
22	Decyl	Methoxy	85.0	130.0
23	Dodecyl	Methoxy	80.0	130.5
24	Tetradecyl	Methoxy	81.0	120.5
25	Hexadecyl	Methoxy	85.0	114.0
26	Octadecyl	Methoxy	80.0	107.0

^a Values in the parentheses indicate monotropy.

much depressed compared with the unsubstituted series.⁵ This behavior is quite unusual. Introduction of a lateral substituent like chloro or methyl with a smaller size show reduction in melting points.

Series B: 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzylidene-4''-toluidines.

Series (A) is non-mesogenic, hence it was proposed to increase the length-to-breadth ratio so that it may exhibit mesomorphism. The aldehydes of series (A) were condensed with *p*-toluidine. The resultant Schiff bases are longer and

more polarizable than the molecules of series (A). As envisaged, the Schiff bases are mesogenic in nature. All the members exhibit nematic mesophase, the first and the last members are monotropic in nature. Smectic mesophase does not commence even in the last member of the series, whereas in the case of the corresponding unsubstituted series 4(4'-*n*-alkoxybenzoyloxy) benzyldene-4"-toluidines (series D), the smectic mesophases commence at the heptyloxy derivative.⁶

The nematic-isotropic transition temperature curve falls steeply and exhibits its usual odd-even effect (Figure 1).

Series C: 4(4'-*n*-Alkoxybenzoyloxy)-3-methoxy benzyldene-4"-anisidines.

Synthesis of series (B) has confirmed that by increasing the length and the polarizability, the molecules of series (A) shows mesomorphism. The molecules of series (B) has alkyl end group. Series (C) was synthesized to determine the effect of an alkoxy group on the mesomorphic nature. Here also, all the derivatives are purely nematic and are enantiotropic in nature. Dave and Kurian⁶ have studied a corresponding unsubstituted homologous series 4(4'-*n*-alkoxybenzoyloxy) benzyldene-4"-anisidines (Series E) and observed that all the members exhibit mesophases of high thermal stabilities and the smectic mesophases commence from the dodecyl member of the series.

The nematic-isotropic transition temperatures show odd-even effect up to the propoxy derivative (Figure 2), whereas, normally the odd-even effect is observed up to the heptyloxy or nonyloxy derivative of the series.

For both the series (B) and (C) it was anticipated that they would exhibit lower crystal-mesomorphic transition temperatures, but the comparison with series (D) and (E) indicates that there is not much difference between these values. Van Meter,⁷ Arora¹ and Gardlund² could obtain low melting liquid crystals by introducing halogen and methyl substituent in the mesogenic homologous series exhibiting broad mesophases.

Table II summarizes the crystal-nematic or isotropic-nematic transition temperatures of series (B) and (C) and the crystal-nematic and smectic-nematic transition temperatures of series (D) and (E).

Reference to Table II indicates that eventhough the crystal-mesomorphic transition temperatures are not depressed in the case of series (B) and (C), the crystal-nematic transition temperatures are quite low compared with those of series (D) and (E) due to the absence of smectic mesophase (the difference is of 27° to 70°C). However, the average decrease in the melting point is not marked and is almost the same as series (D) and (E). This is quite surprising because increase in the breadth and deviation from the acoplanarity due to the steric forces normally decrease the melting points of the system. The behavior of these series suggests that the geometry of the molecules may be such that in

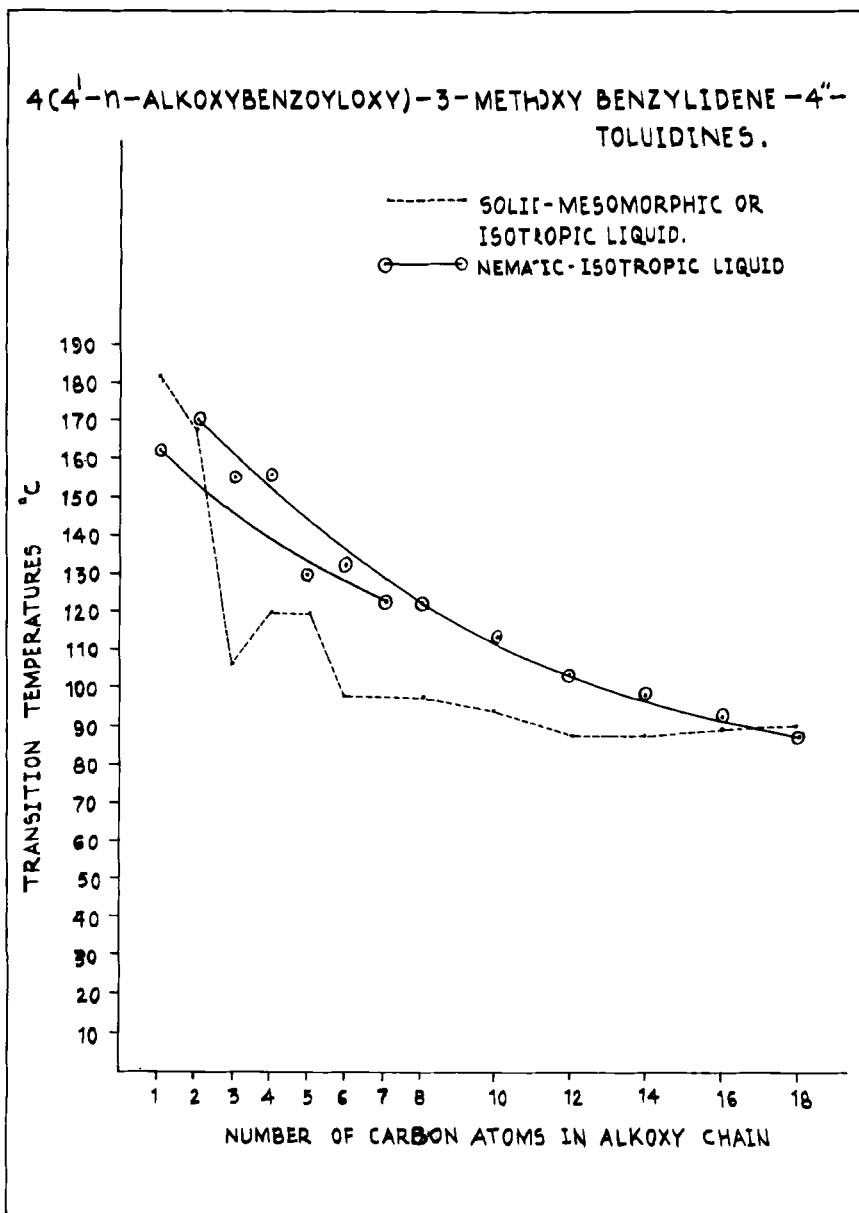


FIGURE 1

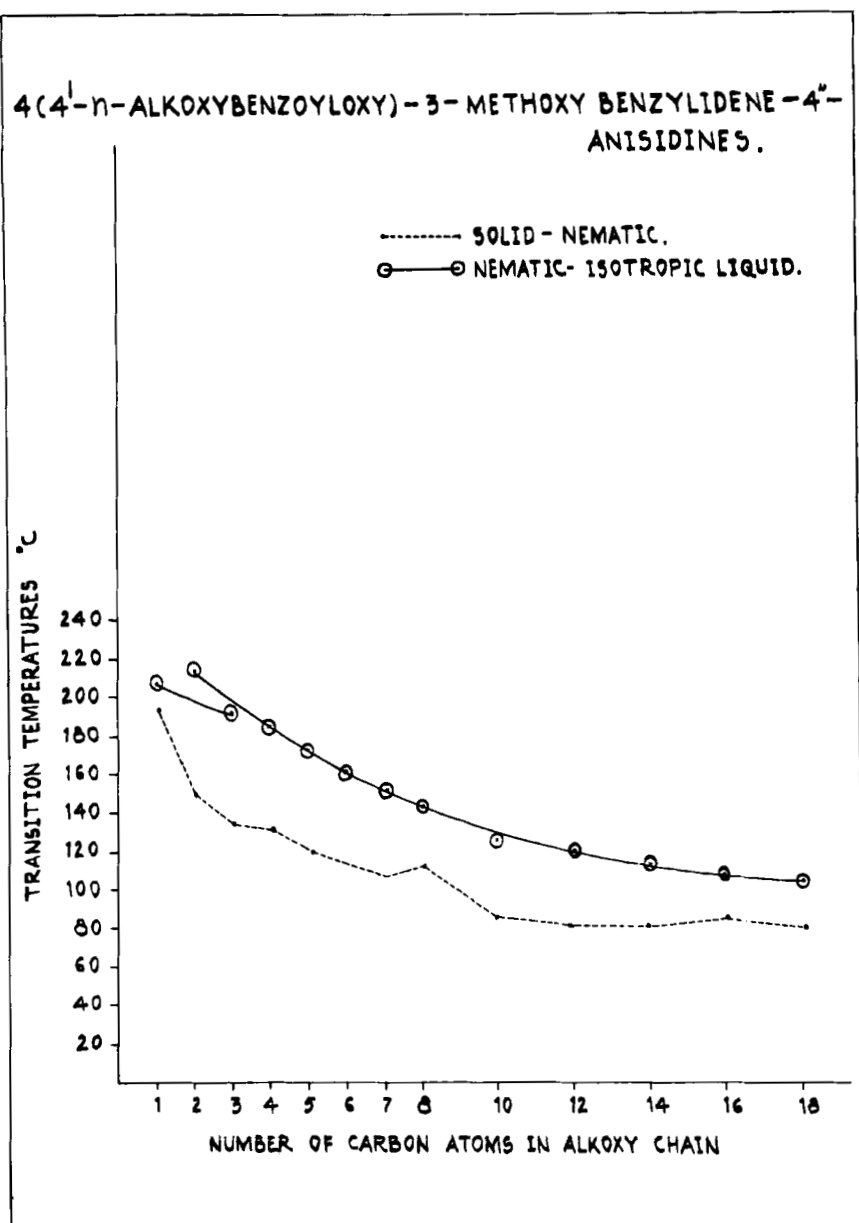


FIGURE 2

TABLE II

Alkoxy Substituent	Series B Crystal-nematic or Isotropic-nematic	Transition Temperatures Series C Crystal-nematic	°C	
			Series D Crystal-nematic or Smectic-nematic	Series D Crystal-nematic or Smectic-nematic
Propyl	105.0	135.0	136.0	125.0
Butyl	120.0	131.0	124.0	118.5
Pentyl	121.0	119.5	119.5	121.0
Decyl	94.0	86.0	121.5	112.0
Dodecyl	88.0	80.0	142.5	116.0
Tetradecyl	88.0	81.0	155.0	118.0
Hexadecyl	90.0	85.0	160.0	130.0
Octadecyl	87.0	80.0	159.5	145.0

solid crystalline phase the lateral methoxy group finds a pocket and hence the melting point does not get depressed, whereas, in the nematic-mesophase molecules are arranged almost parallel and hence the lateral methoxy group will encourage repulsions between the molecules compared with the unsubstituted series. This could be the reason as the nematic-isotropic transitions are drastically reduced. However, the detail X-ray studies can throw light on the packing of the molecules in the crystalline and liquid crystalline phases.

An additional advantage of the series (B) and (C) is the supercooling tendencies of the nematic mesophases. All the members of both the series crystallize well below their crystal-nematic transition temperatures. In case of series (B), some members crystallize at 40–50°C, while in series (C) C₇ and C₈ derivatives crystallize at about 45–50° and 32–33°C respectively. This property increases the potentiality of the compounds for the utility value as the additives to low melting mesogens and to increase nematic mesophase ranges.

The average nematic-isotropic thermal stabilities of the series (B) and (C) are compared with those of series (D) and (E) respectively. (Table III).

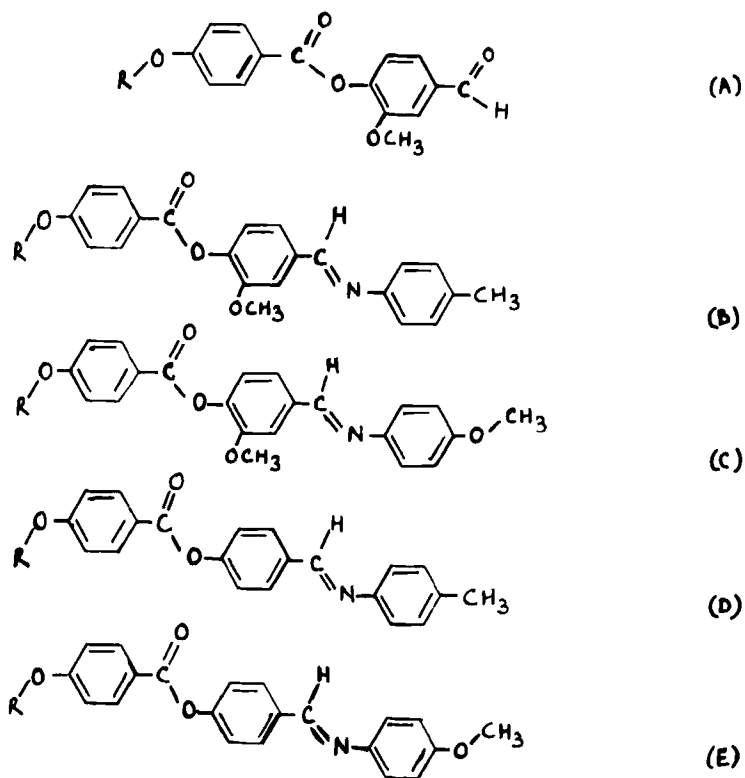
The molecular geometry of these series is given in Figure 3.

It can be seen from the Table III that the nematic-isotropic thermal stabilities of the series (B) and (C) are much lowered (about 95°C) compared with those of series (D) and (E) respectively. Not only this, the nematic mesophase

TABLE III
Average Thermal Stabilities °C

Series	B	C	D	E
Nematic- Isotropic (C ₁ —C ₁₈)	125.4	148.5	220.6	243.6

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MOLECULAR GEOMETRY OF DIFFERENT SERIES.

FIGURE 3

ranges are also much decreased. All the groups are similar except the lateral methoxy group in series (B) and (C). The lateral methoxy group ortho to the ester linkage will have two fold effects on the geometry of the molecules of the present series (B) and (C) (a) of increasing the breath of the molecules and (b) of reducing the co-polarity of the molecules. Both these effects would decrease mesomorphic thermal stabilities. This explains the decrease in nematic thermal stabilities and the absence of smectic mesophase as smectic mesophase would be affected more.

These are the first mesogenic homologous series with bulky methoxy group as a lateral substituent. To study the effect of lateral methoxy group in more detail in our future study we are planning to shift the lateral methoxy group from the central phenyl ring to the end phenyl ring.

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