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R. A. Vora [a] & D. N. Patel [a]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, M. S. University of Baroda, Post Box No. 51, Kalabhavan, Vadodara, 390001, India

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Mesogenic Homologous Series Containing Chloro Group as Ortho and Para Substituent

R. A. VORA and D. N. PATEL

Applied Chemistry Department, Faculty of Technology and Engineering, M. S. University of Baroda, Post Box No. 51, Kalabhavan, Vadodara 390001, India.

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Two mesogenic homologous series 4(4′-*n*-alkoxy benzoyloxy benzylidene)-4″-chloroanilines and 2″-chloroanilines are synthesized. All the members of both the series are mesogenic in nature. Series having terminal chloro substituent is highly smectogenic. Smectic mesophase commences from the propoxy derivative and dodecyloxy derivative onwards all the members exhibit only smectic mesophase. In the case of the series where chloro group is ortho to azomethine linkage, the smectic mesophase commences from hexadecyl derivative. Melting points and transition temperatures of series having terminal chloro group are higher than that of the ortho substituted one. The thermal stabilities of both the series are compared with other structurally related homologous series.

INTRODUCTION

Homologous series of Schiff bases having two benzene rings and a terminal halogen group have been reported.[1-3] These series are less mesogenic and almost half of the members are non-mesogenic. However, it would be quite interesting to incorporate the Schiff base linkages and a chloro group in a system having one more phenyl ring and to study its mesogenic behaviour.

With this in view, two homologous series 4(4′-*n*-alkoxy-benzoyloxy)benzylidene-4″-chloroanilines (A) and 4(4′-*n*-alkoxy benzoyloxy) benzylidene-2″-chloroanilines (B) have been synthesized and their mesogenic properties are studied.

EXPERIMENTAL

4(4′-*n*-alkoxy benzoyloxy)benzaldehydes

4-*n*-alkoxy benzoic acids,[4] 4-*n*-alkoxy benzoylchlorides[4] and 4(4′-*n*-alkoxy benzoyloxy) benzaldehydes[5] were synthesized by known methods and their melting points and transition temperatures agree well with the reported values.

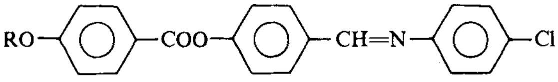
4(4′-*n*-alkoxy benzoyloxy benzylidene) 4″-chloro and 2″-chloro anilines

The Schiff bases were prepared by condensing appropriate 4(4′-*n*-alkoxybenzyloxy) benzaldehyde with 4-chloro aniline and 2-chloroaniline in alcohol. The Schiff bases separated are filtered and recrystallized from ethyl acetate till constant transitions temperatures were obtained. The analytical data of all the members is satisfactory.

Determination of transition temperatures

Transition temperatures of all the compounds were determined by using a polarizing microscope fitted with a FP-2 heating stage. Transition temperatures are recorded in Tables I and II.

TABLE I

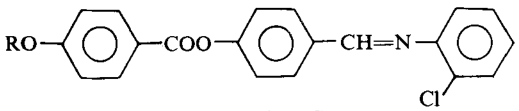


R=*n*—alkyl C_1—C_{16}

Sr. No.	R *n*-alkyl group	Transition temperatures °C Smectic	Nematic	Isotropic
1	Methyl	—	165.0	274.0
2	Ethyl	—	167.0	290.0
3	Propyl	(146.0)[a]	157.0	255.0
4	Butyl	145.0	177.0	264.5
5	Pentyl	135.0	192.0	242.0
6	Hexyl	130.0	208.0	249.0
7	Heptyl	128.5	221.0	240.0
8	Octyl	127.0	223.0	237.5
9	Decyl	127.0	224.5	227.5
10	Dodecyl	122.0	—	224.0
11	Tetradecyl	117.5	—	218.5
12	Hexadecyl	116.0	—	214.0

[a] Value in the parenthesis indicates monotropy.

TABLE II



R=*n*-alkyl C_1—C_{16}

Sr. No.	R *n*-alkyl group	Transition temperatures °C Smectic	 Nematic	 Isotropic
1	Methyl	—	(120)[a]	133.0
2	Ethyl	—	(137.0)	148.0
3	Propyl	—	(116.5)	118.5
4	Butyl	—	107.0	122.0
5	Pentyl	—	90.0	115.0
6	Hexyl	—	109.0	117.0
7	Heptyl	—	102.0	113.5
8	Octyl	—	96.0	115.5
9	Decyl	—	92.0	111.5
10	Dodecyl	—	94.0	109.0
11	Hexadecyl	81.0	93.5	97.0

[a] Values in the parentheses indicate monotropy.

RESULTS AND DISCUSSION

4(4′-*n*-alkoxybenzoyloxy)benzylidene 4″-chloroanilines: Series A

All the members of the series are mesogenic. First two members exhibit nematic mesophase. The smectic mesophase commences from the propoxy member of the series as a monotropic phase. The propoxy to decyloxy derivatives are polymesogenic, exhibiting smectic and nematic mesophases. The dodecyloxy onwards all the members exhibit only smectic mesophase. The series has smectogenic tendencies. The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits odd-even effect (Figure 1) for the nematic–isotropic transition temperatures.

The nematic–isotropic transition temperature curves exhibit falling tendency. The smectic–nematic transition temperature curve does not exhibit odd-even behaviour. In some of the mesogenic homologous series smectic-nematic transition temperature curve exhibits odd-even effect.[6,7] The absence of odd-even effect in the series A for the smectic–nematic transition temperature curve may probably be due to the steep rise of smectic–nematic transition temperature curve. To observe the odd-even effect in such a rising curve, it should be of large magnitude.

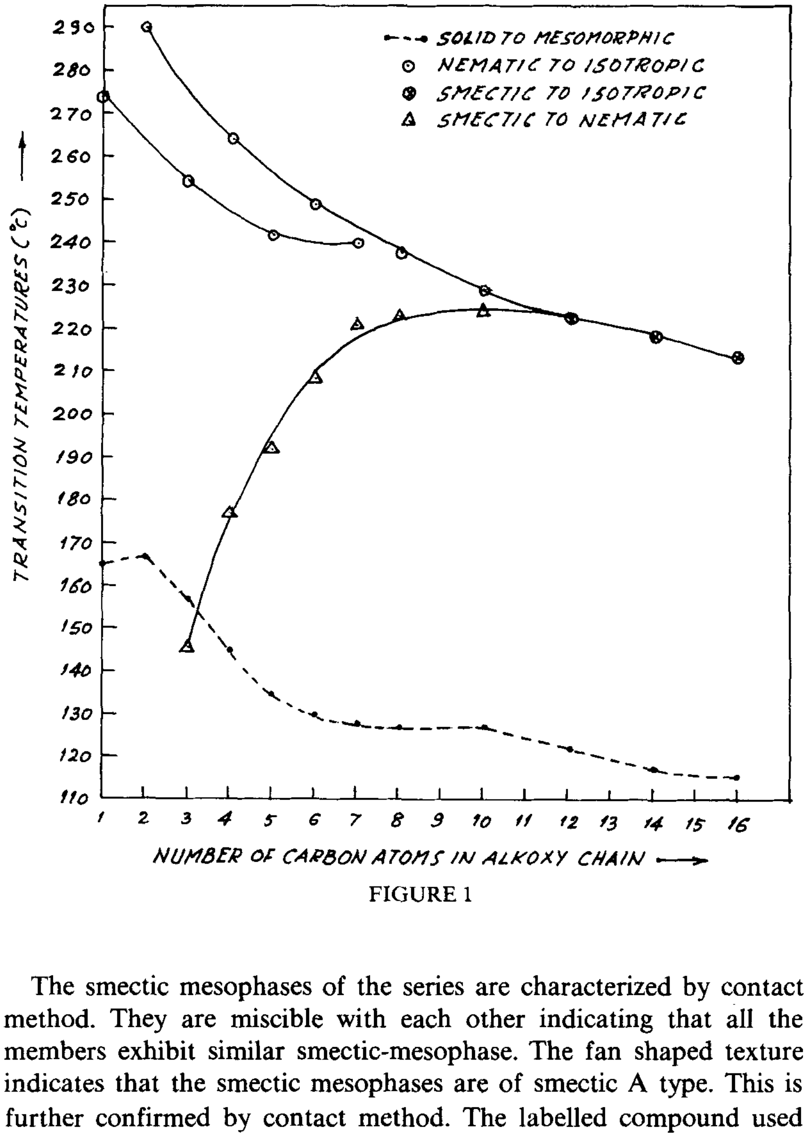


FIGURE 1

The smectic mesophases of the series are characterized by contact method. They are miscible with each other indicating that all the members exhibit similar smectic-mesophase. The fan shaped texture indicates that the smectic mesophases are of smectic A type. This is further confirmed by contact method. The labelled compound used was 4(4′-*n*-hexyloxy benzoyloxy) benzylidene 2″-aminophenol exhibiting smectic A mesophase.[8]

4(4′-*n*-alkoxybenzoyloxy)benzylidene-2″-chloroanilines: Series B

All the members are mesogenic in nature. The methoxy to propoxy derivative exhibit monotropic nematic mesophase. The butoxy to dodecyloxy derivatives exhibit enatiotropic nematic mesophase. The hexadecyloxy derivative exhibits smectic and nematic mesophases. The

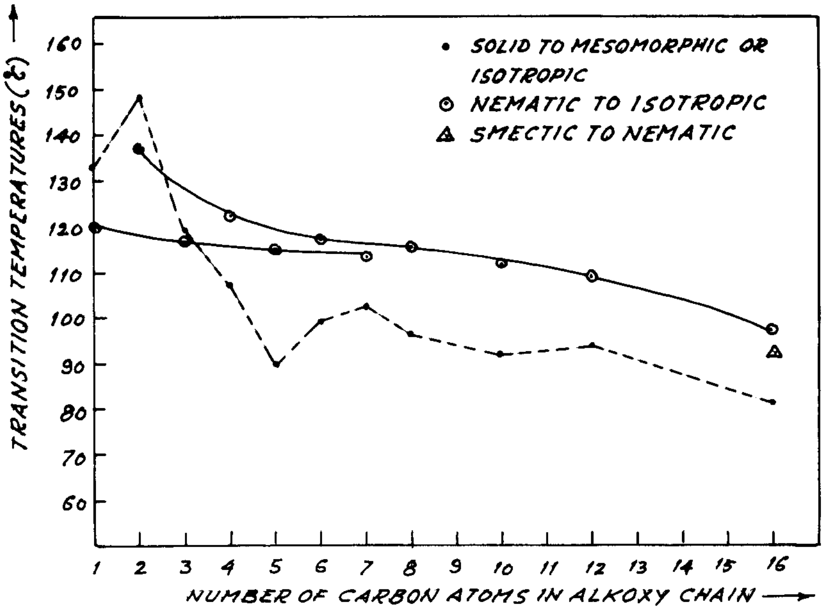


FIGURE 2

plot of transition temperatures versus number of carbon atoms in the alkoxy chain (Figure 2) exhibits odd-even effect for the nematic–isotropic transition temperatures.

The average transition temperatures of both the homologous series A and B are compared with the following homologous series (Table III).

TABLE III

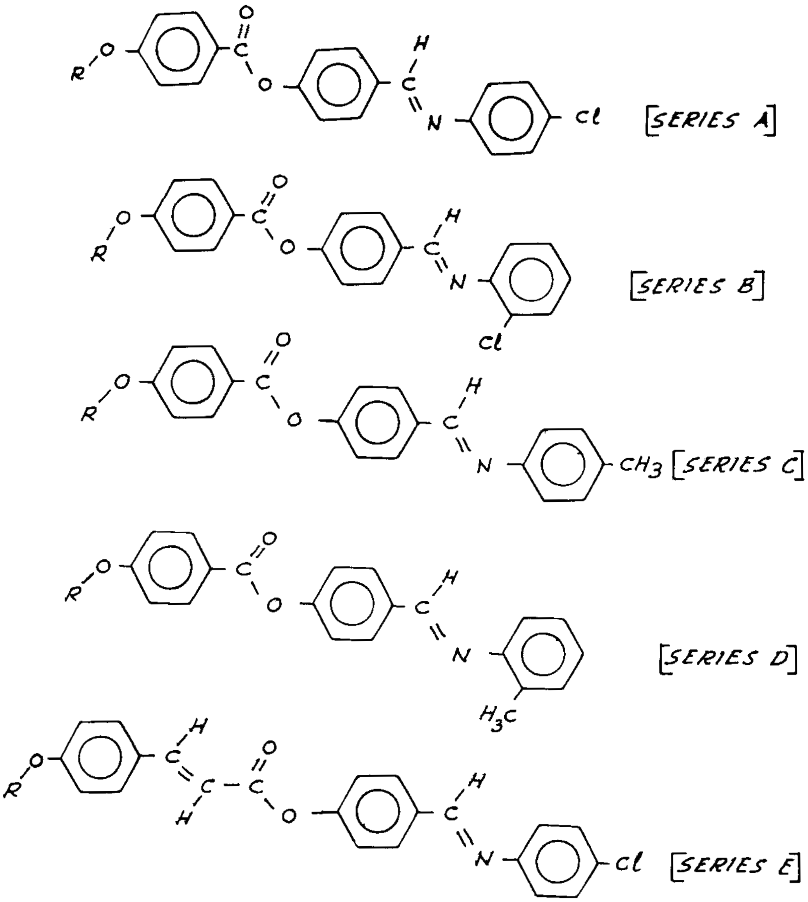
Average thermal stabilities

Phase transitions °C	Series				
	A	B	C	D	E
Smectic to Nematic or Isotropic transitions C_8—C_{16}	221	93.5 C_{16}	129.8	86	233
Nematic to Isotropic C_1—C_{16}	253 C_1—C_{10}	117	220	116	276 C_1—C_{12}
Commencement of smectic phase	C_3	C_{16}	C_7	C_8	C_4

1. 4(4′-*n*-alkoxybenzoyloxy)benzylidene-4″-toluidines—(C)(5).
2. 4(4′-*n*-alkoxybenzoyloxy)benzylidene-2″-toluidines—(D)(9).
3. 4(4′-*n*-alkoxycinnamoyloxy)benzylidene-4″-chloroanilines—(E) (9a).

The geometry of all the homologous series are given in Figure 3.

Reference to table III shows that the thermal stabilities of series B are much lower compared with those of series A. The reference to Figure 3 clearly indicates that all other groups and linkages are same in both the series but they differ only in the respect of substituent present in the phenyl ring at one end. In the case of series A chloro



GEOMETRY OF THE SERIES

FIGURE 3

group is as terminal substituent (para position), whereas in the case of series B same substituent is present in ortho position. It is known that the terminal halogen group will enhance end to end cohesive forces and lateral cohesive forces resulting in higher thermal stabilities, whereas in the case of series B the lateral chloro substituent will have its detrimental effect on mesophases as it increases the breadth of the molecules compared to series A, moreover as it is ortho to Schiff base linkage, to reduce the steric effect, molecules of series B, will be more accoplanar.[10] Both these factors will reduce smectic as well as nematic thermal stabilities. However the reduction in smectic thermal stabilities is a little less than that in nematic thermal stabilities. This is contrary to normal behaviour. Normally increase in breadth and accoplanarity has more pronounced effect on smectic thermal stabilities than on the nematic thermal stabilities.

The difference between series A and C is only in the terminal group. Series C has a methyl terminal substituent whereas series A has chloro terminal substituent. Earlier studies have shown that the effect of chloro and methyl group is almost similar due to their almost equal size in mixed liquid crystalline studies.[11]

The nematic thermal stabilities of series A is higher than those of series C. This can be attributed to the higher polarity which in turn will increase end to end cohesive forces leading to thermal stabilities. The smectic thermal stabilities of series A are much more enhanced compared to series C.

In a normal way end halogen group, due to end to end interaction would enhance nematic mesophase more than the smectic mesophase as the strong dipolar interactions of terminal group should make layer arrangement more unstable. Gray[12] has pointed out that in such dipolar interactions finally a tilted arrangement of the molecules results, where attractive and repulsive forces are quite balanced. This explains enhanced smectic thermal stabilities of series A. This factor also helps in the early commencement of the smectic mesophase in series A. Normally in a nematogenic homologous series smectic mesophase appears in the middle members where lateral cohesive forces are sufficiently enhanced by the longer alkoxy chain. However, in series A, the smectic mesophase commences from the propoxy derivative and in series C it commences from the heptyloxy derivative. As discussed above the layer arrangement is favoured in series A compared to series C, which helps in the early commencement of the smectic mesophase.

Series B and D differ only in the lateral substituent. Series B has a chloro group ortho to Schiff-base linkage whereas series D has a methyl substituent in that position. The size of two groups is almost equal as stated above, hence both the series should have almost identical mesogenic behaviour. Reference to Table III shows that both the series have almost-equal nematic and smectic thermal stabilities. However, the striking difference is in smectogenic tendencies. Series B is least smectogenic, whereas smectic mesophase commences from the octyloxy derivative in series D. This is exactly opposite trend than the one observed between series A and C, which also have similar differences. Series A, having a halogen end group has enhanced smectogenic tendencies compared to series C having a methyl group. In the case of series A, terminal dipolar interactions enhance smectic tendencies and thermodynamic stabilities. The situation will be different in the case of series B. The intermolecular and intramolecular steric interactions will be almost similar in series B and D as the size of the two groups is almost-equal. However, the dipolar interactions of chloro group will have added effects. The chloro group will have intramolecular as well as intermolecular dipolar interactions due to its ortho position to Schiff base linkage. Intermolecular interactions will not allow close packing of the molecules possible whereas intra-molecular interactions between Schiff-base linkage and chloro group will enhance the acoplanarity of the molecules. Both these factors are highly deterrent to smectic mesophase, naturally the commencement of the smectic mesophase will be delayed in Series B. The early commencement of smectic mesophase in Series D has been explained by proposing a model where methyl group finds a pocket in the layer hence the commencement of the smectic mesophase is not much delayed.[9] This is not possible in the case of series B as stated above due to the added dipolar interactions. The thermal stabilities of series E are higher compared to those of series A. This is expected as the molecules of series E are little longer and more polarizable due to the presence of —CH=CH-linkage. Though the thermal stabilities of series E are higher than those of series A, the smectic mesophase does not commence very early in series E. This can be attributed to the breadth increasing effect of —CH=CH-linkage due to its trans conformation.

The foregoing discussion suggests that the therminal halogen group enhances smectic mesophase (series A) more compared to methyl group whereas the same substituent has deterrent effect on smectic mesophases in lateral position compared to methyl group as observed in series B.

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