INFLUENCE OF MOLECULAR STRUCTURE ON LIQUID CRYSTALLINE PROPERTIES AND PHASE TRANSITIONS IN THESE STRUCTURES, PART I

BY

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Figures in this paper correspond to the Figures in the Thesis as under :

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Influence of Molecular Structure on Liquid Crystalline Properties and Phase Transitions in These Structures Part I +

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Abstract - Three homologous series of Schiff's base compounds have been prepared to investigate the relationship between chemical constitution and mesomorphism, by condensing p-n-alkoxybenzaldehydes with p-n-propoxy-, p-n-butoxy- and p-n-amyloxyanilines respectively and the various transition temperatures are recorded. These series exhibit the general mesomorphic properties as found in other analogous series. It is found that the lower homologues are either non-mesomorphic or nematic while middle members are smectic and nematic both and the higher homologues are purely smectic. In many homologues polymesomorphism in smectic phase is observed.

A number of homologous series[1-7] of organic compounds having a variety of molecular structures have been prepared to investigate the relationship between chemical constitution and mesomorphism. It has been observed that, when the alkyl chains are short, the systems are either non-mesomorphic or nematic; as the chain length increases, smectic properties

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begin to appear and as the smectic phase increases, the nematic phase decreases with each successive chain increment, till in the higher homologues like hexadecyl and octadecyl ethers only smectic phases are found; of course, it is not possible to postulate very accurately the stage at which smectic properties would first appear in a particular series.

In the present study, the following three series have been prepared and their various transition temperatures are summarized in Tables 1, 2 and 3 respectively:

I p-n-Alkoxybenzylidene-p-n-propoxyanilines

II p-n-Alkoxybenzylidene-p-n-butoxyanilines

III p-n-Alkoxybenzylidene-p-n-amyloxyanilines

When these values for various transitions are plotted against the number of carbon atoms in the alkoxy chain, the curves represented in Figs. 1, 2 and 3 are obtained for the respective series.

Observation and Discussion

In these three series, all the mesomorphic-isotropic transitions relating to even number of C-atoms in the alkoxy chain lie on one falling curve while similar transitions relating to odd number of C-atoms in the alkoxy chain lie on a curve which rises from C_1-ether to C_7-ether and then falls or shows a falling tendency from C_7-ether to C_9-ether. However, the curve representing these transitions for even number of C-atoms in the chain lies above the one for the same transitions for odd number of C-atoms in the chain. All smectic-nematic transition points, irrespective of odd or even number of C-atoms in the chain, lie on one smooth rising

TABLE - 1

Series I : p-n-Alkoxybenzylidene-p-n-propoxyanilines

Alkyl group	Temperature of transition to			
	$Smectic_2$	$Smectic_1$	Nematic	Isotropic
1. Methyl	-	-	(102.0)[a]	119.5
2. Ethyl	-	-	(125.0)	127.5
3. Propyl	-	-	(104.0)[a]	134.5
4. Butyl	-	-	(115.0)[b]	121.0
5. Amyl	-	-	104.5	105.5
6. Hexyl	-	-	98.0	110.0
7. Heptyl	-	-	102.0	107.0
8. Octyl	-	-	100.5	108.0
9. Nonyl	-	(96.5)	105.0	107.0
10. Decyl	(88.5)	(100.0)	103.5	106.7
11. Dodecyl	(91.0)	(103.0)	(104.7)	106.0
12. Hexadecyl	-	(101.5)	-	104.5
13. Octadecyl	-	(100.0)[a]	-	108.5

a Values obtained by extrapolating the curve.

b Values in the bracket indicate monotropy.

TABLE - 2

Series II : p-n-Alkoxybenzylidene-p-n-butoxyanilines

Alkyl group	Temperature of transition to			
	$Smectic_2$	$Smectic_1$	Nematic	Isotropic
1. Methyl	-	-	(108.5)	115.0
2. Ethyl	-	-	111.0	131.5
3. Propyl	-	-	(114.5)	120.0
4. Butyl	-	-	(122.0)	125.0
5. Amyl	-	-	(115.0)	116.5
6. Hexyl	-	-	102.5	118.5
7. Heptyl	-	-	100.5	115.5
8. Octyl	-	(98.5)	105.0	115.0
9. Nonyl	-	102.0	104.5	113.5
10. Decyl	(92.5)	104.0	108.5	113.0
11. Dodecyl	(95.0)	101.0	111.0	111.5
12. Hexadecyl	-	101.5	-	107.0
13. Octadecyl	-	(104.5)	-	107.5

TABLE - 3

Series III : p-n-Alkoxybenzylidene-p-n-amyloxyanilines

Alkyl group	Temperature of transition to				
	Smectic$_3$	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
1. Methyl	-	-	-	(101.0)[a]	108.0
2. Ethyl	-	-	-	96.0	121.0
3. Propyl	-	-	-	(105.5)[b]	107.5
4. Butyl	-	-	-	(114.0)	115.5
5. Amyl	-	-	-	(108.5)[a]	114.5
6. Hexyl	-	-	-	104.0	113.0
7. Heptyl	-	-	94.0	98.5	110.0
8. Octyl	(84.0)	91.0	100.5	102.0	111.2
9. Nonyl	(88.5)	-	95.5	104.5	109.7
10. Decyl	(91.0)	94.5	105.5	107.0	109.5
11. Dodecyl	(93.0)	98.0	105.0	-	108.0
12. Hexadecyl	-	(94.5)	98.5	-	105.0
13. Octadecyl	-	-	(103.5)	-	106.0

a Values obtained by extrapolsting the curve.

b Values in the bracket indicate monotropy.

curve which merges with the falling nematic-isotropic curve for the even members. Smectic$_1$-smectic$_2$ transition points also lie on one curve.

Methyl, propyl and octadecyl ethers in the first series are not mesomorphic but the isotropic-nematic transition values can be obtained by extrapolating the respective curves in a legitimate fashion. When the isotropic

Fig. 1. The plot of transition temperatures of series I.

liquid of methyl, propyl and octadecyl ethers is cooled, crystallization takes place at 108°, 129° and 103.5°C respectively, before giving any mesophase. Weygand and Gabler[1] have reported that p-n-propoxybenzylidene-p-n-propoxyaniline melts at 133°C and they have given the calculated value of 107° for isotropic-nematic change. We, however, find that

Fig. 2. The plot of transition temperatures of series II.

this compound melts at 134.5°C and the value 107°C is 3° higher than the value obtained by us by extrapolation of the curve for odd members of this series. In this series, smectic phase is found throughout in the undercooled region and has failed to become enantiotropic.

All the members of the p-n-alkoxybenzylidene-p-n-butoxyaniline series are crystalline liquids - methyl, propyl, butyl, amyl and octadecyl derivatives being purely monotropic. Hexadecyl ether is purely enantiotropic smectic and octadecyl

ether is purely monotropic smectic. The smectic property

Fig. 3. The plot of transition temperatures of series III.

starts from octyl ether unlike nonyl ether of series I. The transition temperatures of p-n-butoxybenzylidene-p-n-butoxyaniline agree with the values given by Weygand and Gabler[1].

In the series p-n-alkoxybenzylidene-p-n-amyloxyanilines, methyl and amyl ethers are non-mesomorphic but when the curve passing through nematic-isotropic transitions for the members having odd number of C-atoms in the chain, is drawn and extrapolated towards short carbon chain ethers, it gives 101 ^{o}C for isotropic-nematic change of methyl ether and 108.5 ^{o}C for the similar transition of amyl ether. When the isotropic liquid of methyl and amyl ether is cooled, crystallization takes place at about 102.5 ^{o}C and 110.0 ^{o}C respectively before giving isotropic-nematic transition. Weygand and Gabler[1] however, give transition temperatures for p-n-amyloxybenzylidene-p-n-amyloxyaniline as (103.0 ^{o})-113.0 ^{o}C.

Weygand and Gabler[1] have studied mesomorphism of p-n-alkoxybenzylidene-p-phenetidine compounds. The series studied here are the higher homologues of this series and naturally similar properties should be expected. In all these series, lower homologues are non-mesomorphic or nematic (either monotropic or enantiotropic) while middle members are both smectic and nematic and the higher homologues like

hexadecyl and octadecyl ethers are purely smectic (either enantiotropic or monotropic). It is rather difficult to postulate where the smectic properties should originate in the series, however, in the three series studied here, some regularity regarding the appearance of the smectic phase is observed. In the propyl-ether series, smectic phase first appears at C_9-ether while in butyl-ether and amyl-ether series, the smectic properties begin at C_8- and C_7-ethers respectively. On this basis, one may expect that in the ethyl-ether series, smectic phase should appear at C_{10}-ether, but as a matter of fact, in ethyl-ether series[1] smectic phase appears at C_9-ether.

As the chain length is increasing, the terminal cohesive forces which account for nematic-isotropic change decrease, as a result of which the nematic-isotropic curve obtained for even-members in these series is a falling one. Similar curve should also be obtained for odd-members but in practice, a rising curve is obtained which shows a falling tendency from C_7-ether to C_9-ether. This may probably be due to relative differences between the terminal and lateral cohesions. As the chain length increases, lateral cohesion increases and it may support the terminal forces; this to a certain degree, helps in explaining the rise in the curve which afterwards shows the tendency of becoming a normal falling curve. Still, it is a matter of curiosity as the odd members behave in one way and the even members in the other way. Probably this difference may be due to differences in packing and cohesion between the terminal methyl groups of alkyl chains containing odd and even

number of carbon atoms. Here, in these anils two alkoxy groups of different lengths are present, one on each end, and the study of the mode of their end to end arrangement in the crystal lattice may probably help in explaining this type of behaviour. In the middle members (e.g. nonyl to dodecyl ethers in series I, octyl to dodecyl ethers in series II and heptyl to decyl ethers in series III) as the strength of the terminal intermolecular cohesions decreases, the net polarizability of the molecule increases by increasing chain-length and so lateral intermolecular attractions which account for smectic-nematic transition also increase resulting into increasing smectic-nematic transition temperatures up to a stage, where no nematic phase is formed (e.g. hexadecyl ether of series I and II and dodecyl ether of series III). Later, naturally the higher homologues should be purely smectic as the terminal intermolecular attractions become insufficient to maintain parallel molecular orientation necessary for nematic transformation. Of course, after the stage at which smectic-nematic transition disappears, the smectic-isotropic transition must be guided by the weaker terminal attraction, because in practice, it is found that the smectic-nematic transition curve merges with the falling nematic-isotropic curve for even number of carbon atoms in the chain of a homologous series. If the melting points show a rising tendency, the system may become monotropic as found in dodecyl and hexadecyl ethers of series I and in octadecyl ethers of series II and III, or may become non-mesomorphic as in octadecyl ether of series I. Quite analogous phenomenon

is shown by p-n-alkoxybenzylidene-p-phenetidine compounds.[1]

One more striking behaviour of these series is the polymesomorphism of smectic phases in at least some higher homologues. In the case of series I and II only decyl and dodecyl ethers exhibit smectic$_1$-smectic$_2$ transitions and so, it is very difficult to understand the nature of the curve passing through these points, but in series III, five members, e.g. octyl, nonyl, decyl, dodecyl and hexadecyl ethers show smectic$_1$-smectic$_2$ and smectic$_2$-smectic$_3$ transitions and hence it has become possible to understand the nature of this curve. Smectic$_1$-smectic$_2$ transition curve rises from octyl to decyl ether and then falls through dodecyl ether to hexadecyl ether while smectic$_2$-smectic$_3$ transition points constitute a rising curve. This behaviour suggests that polymesomorphic transitions among smectic mesophases take place at some definite temperature with certain regularity as the homologous series is ascended.

Comparison of the average nematic thermal stability for butyl to nonyl ethers of the series p-n-alkoxybenzylidene-p-n-alkoxyanilines, give the following order :

Series	$-OC_2H_5$	>	$-OC_4H_9$ (II)	>	$-OC_5H_{11}$ (III)	>	$-OC_3H_7$ (I)
Average temps for nematic-isotropic transition (C_4-C_9)	120.5		116.6		111.1		108.7

This order emphasizes the falling nature of the curve passing through nematic-isotropic transition temperatures for the members having even number of carbon atoms in the chain and

rising nature of the curve for the similar transitions for the members possessing odd number of carbon atoms in the chain. From this limited data, one cannot postulate that $-OC_9H_{19}$ series would possess higher nematic thermal stability than $-OC_7H_{15}$ series as it is observed in all the series that the nematic-isotropic curve for odd number of carbon atoms in the chain shows a falling tendency from C_7-ether to C_9-ether.

The order obtained for the smectic thermal stability of the three series examined here is as follows :

Series ...	$-OC_3H_7$ (I)	<	$-OC_5H_{11}$ (III)	<	$-OC_4H_9$ (II)
Average temps.for smectic-nematic or smectic-isotropic transition (C_9-C_{12})	101.6		106.6		108.0

Here again series II shows highest smectic thermal stability like nematic thermal stability among the three series in question. This data also suggests that smectic-nematic curve should rise in the initial state and then fall.

Experimental

Determination of Transition Temperatures

Preliminary measurements were made by the optical method of Dave and Dewar[8]. The precise measurements were however made by the polarizing microscope. To prepare the slide, the specimen was melted on a glass slide and a cover-slip was pressed down on the liquid to get a possible thin section of the material. The slide was inserted in the slide slot of the

TABLE - 4

p-n-Alkoxybenzylidene-p-n-propoxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	5.349	$C_{17}H_{19}O_2N$	5.204
2. Ethyl	4.966	$C_{18}H_{21}O_2N$	4.947
3. Propyl	4.953	$C_{19}H_{23}O_2N$	4.713
4. Butyl	4.686	$C_{20}H_{25}O_2N$	4.501
5. Amyl	4.366	$C_{21}H_{27}O_2N$	4.307
6. Hexyl	4.277	$C_{22}H_{29}O_2N$	4.129
7. Heptyl	4.086	$C_{23}H_{31}O_2N$	3.966
8. Octyl	3.915	$C_{24}H_{33}O_2N$	3.814
9. Nonyl	3.655	$C_{25}H_{35}O_2N$	3.674
10. Decyl	3.664	$C_{26}H_{37}O_2N$	3.544
11. Dodecyl	3.321	$C_{28}H_{41}O_2N$	3.301
12. Hexadecyl	2.843	$C_{32}H_{49}O_2N$	2.923
13. Octadecyl	2.671	$C_{34}H_{53}O_2N$	2.761

TABLE - 5

p-n-Alkoxybenzylidene-p-n-butoxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1.Methyl	4.945	$C_{18}H_{21}O_2N$	4.947
2. Ethyl	4.506	$C_{19}H_{23}O_2N$	4.713
3. Propyl	4.418	$C_{20}H_{25}O_2N$	4.501
4. Butyl	4.065	$C_{21}H_{27}O_2N$	4.307
5. Amyl	3.930	$C_{22}H_{29}O_2N$	4.129
6. Hexyl	3.759	$C_{23}H_{31}O_2N$	3.966
7. Heptyl	3.574	$C_{24}H_{33}O_2N$	3.814
8. Octyl	3.516	$C_{25}H_{35}O_2N$	3.674
9. Nonyl	3.376	$C_{26}H_{37}O_2N$	3.544
10. Decyl	3.415	$C_{27}H_{39}O_2N$	3.423
11. Dodecyl	3.267	$C_{29}H_{43}O_2N$	3.204
12. Hexadecyl	2.647	$C_{33}H_{51}O_2N$	2.840
13. Octadecyl	2.654	$C_{35}H_{55}O_2N$	2.688

TABLE - 6

p-n-Alkoxybenzylidene-p-n-amyloxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	4.974	$C_{19}H_{23}O_2N$	4.713
2. Ethyl	4.333	$C_{20}H_{25}O_2N$	4.501
3. Propyl	4.262	$C_{21}H_{27}O_2N$	4.307
4. Butyl	3.973	$C_{22}H_{29}O_2N$	4.129
5. Amyl	3.883	$C_{23}H_{31}O_2N$	3.966
6. Hexyl	3.634	$C_{24}H_{33}O_2N$	3.814
7. Heptyl	3.793	$C_{25}H_{35}O_2N$	3.674
8. Octyl	3.358	$C_{26}H_{37}O_2N$	3.544
9. Nonyl	3.234	$C_{27}H_{39}O_2N$	3.423
10. Decyl	3.601	$C_{28}H_{41}O_2N$	3.301
11. Dodecyl	3.277	$C_{30}H_{45}O_2N$	3.104
12. Hexadecyl	2.653	$C_{34}H_{53}O_2N$	2.761
13. Octadecyl	2.487	$C_{36}H_{57}O_2N$	2.617

hot-stage fitted Leitz Ortholux polarizing microscope. In this electrically heated block, the sample could be observed continuously under carefully controlled temperatures. The temperature in the neighbourhood of each change was raised at the rate of 1^{0}/ 2 min and the temperatures for various transitions were recorded by the standard thermometers. The transitions were also checked by lowering the temperature slowly and observing the phase changes.

p-n-Alkoxybenzaldehydes were prepared by the method of G.W.Gray.[3] p-n-Alkoxyanilines were prepared by the method of Weygand and Gabler[1] and Gutekunst and Gray.[9]

Schiff's bases : The Schiff's base compounds were prepared by refluxing equimolecular quantities of the corresponding aromatic aldehyde and aniline in alcohol for about 10 to 15 min and recrystallizing the product, several times from ethyl alcohol into fine crystals which give sharp melting point. The analytical data are given in Tables 4 to 6.

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INFLUENCE OF MOLECULAR STRUCTURE ON LIQUID CRYSTALLINE PROPERTIES AND PHASE TRANSITIONS IN THESE STRUCTURES, PART II

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Influence Of Molecular Structure On Liquid Crystalline Properties And Phase Transitions In These Structures, Part II[+]

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Abstract - Thirteen p-n-alkoxybenzylidene-p-aminobenzoic acids were prepared and their mesomorphic transition temperatures were determined. They exhibit mesophases of greater relative thermal stability than the p-n-alkoxybenzoic and p-n-alkoxycinnamic acids but 4'-n-alkoxydiphenyl-4- carboxylic acids exhibit greater thermal stability than the acids studied here though p-n-alkoxybenzylidene-p-aminobenzoic acids are longer by -CH=N- group in the monomer; this may be attributed to the stereo-chemistry of -CH=N- link causing the molecule to be broader than the 4'-n-alkoxydiphenyl-4-carboxylic acids. Comparatively higher thermal stability of mesophases of these acids is emphasized by the mesomorphic behaviour of methyl p-n-alkoxybenzylidene-p-aminobenzoates which are purely smectic and the absence of anisotropic melt in the analogous p-n-alkoxybenzoates.

Liquid crystalline properties of many homologous aromatic carboxylic acid series[1-5] have been studied earlier and their mesomorphic properties are discussed taking into consideration the dimer molecule which is elongated, narrow and possess a

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+ This paper was read at the International Conference of Liquid Crystals held at Kent State University, Kent, Ohio U.S.A., 1965.

TABLE - 1

Series : p-n-Alkoxybenzylidene-p-aminobenzoic acids

Alkyl group	Temperature of transition to Smectic	Nematic	Isotropic
1. Methyl	-	196.5	286.5
2. Ethyl	-	215.0	290.0
3. Propyl	-	190.0	272.0
4. Butyl	-	182.5	273.0
5. Amyl	-	214.0	260.0
6. Hexyl	160.0	172.5	260.5
7. Heptyl	162.0	205.0	251.0
8. Octyl	155.0	216.5	250.0
9. Nonyl	137.5	226.5	244.5
10. Decyl	131.5	231.5	242.0
11. Dodecyl	128.0	-	235.0
12. Hexadecyl	111.0	-	222.0
13. Octadecyl	106.5	-	216.0

TABLE - 2

Series : Methyl p-n-alkoxybenzylidene-p-aminobenzoates

Alkyl group	Temperature (°C) of transition to Smectic	Isotropic
1. Methyl	-	132.5
2. Ethyl	-	127.0
3. Propyl	-	119.0
4. Butyl	96.5	116.5
5. Amyl	79.5	95.0
6. Hexyl	90.0	118.5
7. Heptyl	94.5	117.5
8. Octyl	94.0	120.0
9. Nonyl	101.0	119.5
10. Decyl	99.5	120.0
11. Dodecyl	105.5	118.5
12. Octadecyl	110.5	111.0

polar alkoxy group at each end. In the present work, the series p-n-alkoxybenzylidene-p-aminobenzoic acids and their methyl esters have been synthesized and their various transitions have been studied which are given in Tables 1 and 2 respectively.

p-n-Alkoxybenzylidene-p-aminobenzoic acid series is a potentially mesomorphic series in which all the members are liquid crystalline like trans p-n-alkoxycinnamic acids,[3] 6-n-alkoxy-2-naphthoic acids[2] and 4'-n-alkoxydiphenyl-4-carboxylic acids.[4] Methyl to amyl ethers of this series are purely enantiotropic nematic, hexyl to decyl ethers are both smectic and nematic and dodecyl, hexadecyl and octadecyl ethers are purely smectic - the smectic phase increasing at the cost of nematic phase.

When the transition points are plotted against the number of carbon atoms in the alkyl chain, the transition points relating to the change mesomorphic to isotropic fall on two falling curves, one representing the ethers with odd number of carbon atoms in the alkoxy chain and the other

Fig. 1. The plot of transition temperatures of series I

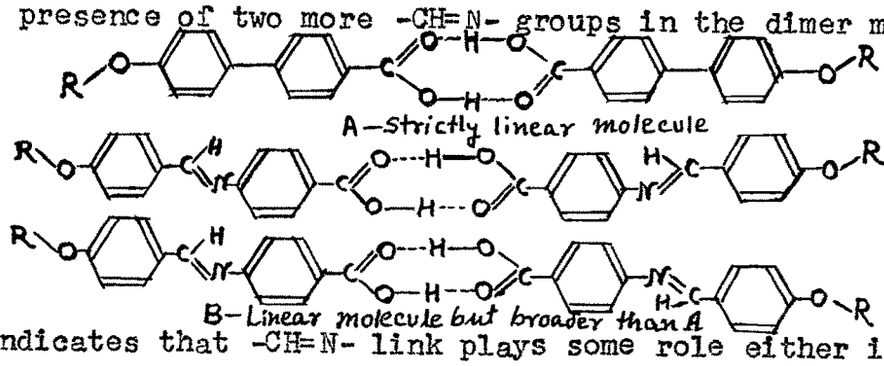
representing the ether with even number of carbon atoms in the alkoxy chain. The latter curve lies above the previous ones. Five smectic-nematic transition points lie on one smooth rising curve; this meets the falling nematic-isotropic curve for even members of the series at C_{12}-ether which does not possess any nematic property: At the points marked with + sign

in Fig. 1, very highly threaded nematic structure sets in, which vanishes soon and cloudy melt remains.

The following table summarizes the average thermal stabilities of smectic and nematic mesophases of the series, viz. p-n-alkoxybenzoic acids (A), trans p-n-alkoxycinnamic acids (B), 6-n-alkoxy-2-naphthoic acids (C), p-n-alkoxybenzylidene-p-aminobenzoic acids (I) and 4'-n-alkoxydiphenyl-4-carboxylic acids (D).

Series	A	B	C	I	D
Average smectic-nematic or smectic-isotropic transition temps. (C_9-C_{10}, C_{12}, C_{16}, C_{18})	126.3	153.6	153.0	226.2	248.9
Average nematic-isotropic transition temps. (C_3-C_{10})	149.5	178.1	195.1	256.6	270.6

Comparison of the average thermal stabilities of these series shows that the average thermal stability of smectic and nematic mesophases of these series increases with the increase of double bonds but in the case of series I and D the former has less thermal stabilities than that of series D, in spite of the presence of two more -CH=N- groups in the dimer molecule.



This indicates that -CH=N- link plays some role either in the packing of the molecules in crystal lattices or due to the stereochemistry of this group, the molecule is not

strictly linear as in the case of 4'-n-alkoxydiphenyl-4-carboxylic acids as shown below. Consequently the thermal stabilities might have decreased though the dimerized molecule is longer than 4'-n-alkoxydiphenyl-4-carboxylic acids.

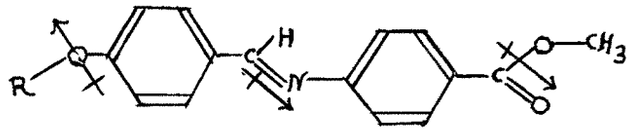
Fig. 2. The plot of transition temperatures of series II

Methyl esters of p-n-alkoxybenzoic acids are trans p-n-alkoxycinnamic acids do not exhibit any mesophase, probably due to reduction in length brought about by esterification of -COOH group which otherwise forms dimerized long molecules in the acid series; but as the methyl esters of 4'-n-alkoxydiphenyl-4-carboxylic acids[4] exhibit mesomorphism, methyl esters of p-n-alkoxybenzylidene-p-aminobenzoic acids were prepared and examined, and in many homologues mesomorphism was observed. The melting points and smectic-isotropic transition points for this methyl ester series are summarized in Table 2 and in Fig.2 these points are plotted against the number of carbon atoms in the alkoxy group.

The mesomorphic homologues of methyl p-n-alkoxybenzylidene-p-aminobenzoate series show only smectic phases - methyl, ethyl and propyl ethers being non-mesomorphic. When mesomorphic-isotropic transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, they constitute two curves - the curve representing even number of carbon atoms in the chain passes through maximum at C_{10}-ether and lies above the other which represents odd number of carbon atoms in the chain and reaches maximum at C_9-ether.

We have seen in other series that purely smectic properties are found only in higher homologues like hexadecyl

and octadecyl ethers; however, in this ester series, even though the molecules are shorter than corresponding acid molecules, purely smectic mesophases are found in short alkyl ethers like methyl p-n-butoxybenzylidene-p-aminobenzoate. This behaviour suggests that -COOR group plays some role for the mesomorphism of this kind. Here, the molecule is narrow and elongated with a terminally situated ester group on one end and alkoxy group on the other end as shown below:



The strong dipole moment of the carbalkoxy group operates at an angle to the long axis of the molecule and may help the molecule to adopt a layer lattice when crystallization takes place and preserves the molecules in the layer arrangement characteristic for smectic mesophases when melting occurs. Of course, the dipole moment of only carbalkoxy group may not be able to cause this phenomenon as indicated by the absence of mesomorphism in methyl benzylidene-p-aminobenzoate; so the dipole moment of the alkoxy group which also acts at an angle to the long axis of the molecule may be necessary to supplement the intermolecular lateral cohesions.

These esters provide an evidence that a smectic-isotropic transition temperature curve can rise to a maximum and then fall as found in propyl 4'-n-alkoxydiphenyl-4-carboxylates.[4] This is exhibited in Fig. 2 where the smectic-isotropic curve rises very steeply from C_5- to C_7-ethers and less steeply from C_7- to C_9-ethers; however, it rises gradually from C_4-to C_8-ethers and falls gradually through C_{10}-, C_{12}- and C_{18}-ethers.

The smectic-isotropic transition temperatures for octyl ether and decyl ether are the same (120°C), so it appears that these two points are the optimum portion of this curve relating to even number of carbon atom in the chain. In the case of ethers having odd number of carbon atoms in the chain C_9-ether shows the maximum smectic-isotropic transition temperature and as the higher homologues like C_{11}-ether and C_{13}-ether have not been studied, the exact nature of this curve cannot be postulated.

The purely smectic mesomorphism found in this series accounts for the relatively high thermal stabilities of mesophases of p-n-alkoxybenzylidene-p-aminobenzoic acids. Moreover, the first member to exhibit mesomorphism in the series methyl 4'-n-alkoxydiphenyl-4-carboxylates is the hexyl ether and in the case of methyl p-n-alkoxybenzylidene-p-aminobensoate series, butyl ether is the first to show smectic properties. This may be attributed to the extra dipole moment due to -CH=N- link acting at an angle to main molecular axis. However, the average smectic thermal stability of this series is less than that of methyl 4'-n-alkoxydiphenyl-4-carboxylates (E) as shown below:

Series	II	E
Average smectic-isotropic transition temperatures. (C_6-C_{12})	119.0	131.8

In fact, it should be expected that the smectic thermal stability of this series should be higher than methyl 4'-n-alkoxydiphenyl-4-carboxylates as the compounds of this series contain one more dipole due to -CH=N- link, acting at an angle to molecular main axis, thus reinforcing the lateral cohesive forces. This is

TABLE - 3

Series : p-n-Alkoxybenzylidene-p-aminobenzoic acids

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	5.557	$C_{15}H_{13}O_3N$	5.490
2. Ethyl	5.101	$C_{16}H_{15}O_3N$	5.204
3. Propyl	4.916	$C_{17}H_{17}O_3N$	4.946
4. Butyl	4.683	$C_{18}H_{19}O_3N$	4.713
5. Amyl	4.683	$C_{19}H_{21}O_3N$	4.501
6. Hexyl	4.341	$C_{20}H_{23}O_3N$	4.307
7. Heptyl	4.194	$C_{21}H_{25}O_3N$	4.129
8. Octyl	3.910	$C_{22}H_{27}O_3N$	3.966
9. Nonyl	4.054	$C_{23}H_{29}O_3N$	3.814
10. Decyl	3.589	$C_{24}H_{31}O_3N$	3.674
11. Dodecyl	3.219	$C_{26}H_{35}O_3N$	3.422
12. Hexadecyl	2.828	$C_{30}H_{43}O_3N$	3.010
13. Octadecyl	2.653	$C_{32}H_{47}O_3N$	2.839

TABLE - 4

Series : Methyl p-n-alkoxybenzylidene-p-aminobenzoates

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	5.299	$C_{16}H_{15}O_3N$	5.204
2. Ethyl	4.712	$C_{17}H_{17}O_3N$	4.946
3. Propyl	4.711	$C_{18}H_{19}O_3N$	4.713
4. Butyl	4.618	$C_{19}H_{21}O_3N$	4.501
5. Amyl	4.404	$C_{20}H_{23}O_3N$	4.307
6. Hexyl	4.189	$C_{21}H_{25}O_3N$	4.129
7. Heptyl	3.944	$C_{22}H_{27}O_3N$	3.966
8. Octyl	3.773	$C_{23}H_{29}O_3N$	3.814
9. Nonyl	3.696	$C_{24}H_{31}O_3N$	3.674
10. Decyl	3.456	$C_{25}H_{33}O_3N$	3.544
11. Dodecyl	3.210	$C_{27}H_{37}O_3N$	3.335
12. Octadecyl	2.701	$C_{33}H_{49}O_3N$	2.761

indicative of the roles a strictly linear molecule and an almost linear molecule can play on mesomorphism.

Experimental

Determination of Transition Temperatures

Various transitions were recorded as in Part I.

Preparation of Compounds

The Schiff's base compounds were prepared as in Part I; the analytical data are given in Tables 3 and 4.

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The authors express their thanks to Prof.S.M.Sethna for his interest in the work. One of us (P.R.P.) is thankful to the Council of Scientific and Industrial Research, New Delhi (India) for the award of Junior Research Fellowship.

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INFLUENCE OF MOLECULAR STRUCTURE ON LIQUID CRYSTALLINE PROPERTIES AND PHASE TRANSITIONS IN MIXED LIQUID CRYSTALS IN THE SMECTIC PHASE

BY

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Figures in this Paper correspond to the Figures in the Thesis as under :

Fig. No. in the Paper	Fig. No. in the Thesis
1	15
2	14
3	13
4	34
5	35

Influence of molecular structure on liquid crystalline properties and phase transitions in mixed liquid crystals in the smectic phase[+]

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Abstract : A number of binary systems have been investigated with ethyl p-azoxybenzoate, a smectic liquid crystal and other non-liquid crystalline solutes. When the mesomorphic-isotropic temperatures of such binary systems are plotted against the mole per cent compositions of the liquid crystalline component, two types of curves : (1) a usual curve where the transition line is depressed regularly and (2) a rising curve exhibiting a maximum, are obtained. The latter type of curves indicates an enhancement in the smectic thermal stability while the former, a decrease in the smectic thermal stability during the course of mixed liquid crystal formation.

Mixed liquid crystalline behaviour of binary mixtures in which one or both the components are nematic liquid crystal has been reported earlier[1-6] and it has been found that such mixtures possess a pronounced ability to form homogeneous nematic melt over a range of temperature and concentration.

+ This paper is accepted for publication in the Indian Journal of Chemistry.

More recently, Arnold and Sackmann[7] have done some work to test the miscibility of liquid crystal phases; two nematic phases of two different compounds are completely miscible and form a homogeneous nematic liquid crystalline region; two smectic phases of two different compounds are likewise miscible forming a homogeneous smectic mesomorphic region, however, smectic phase of one compound and nematic phase of the other are not miscible.

Dave and Dewar[5] and later Dave and Lohar[6] studied extensively binary mixtures in which one component was a nematic liquid crystal and the other a non-liquid crystal. They state that the transition lines of binary systems in the phase diagrams stand as a measure of the tendency of the non-mesomorphic component towards mixed mesomorphism; consequently they obtained different values of group slopes for various end groups. The lower slope value indicates the greater tendency of non-mesomorphic component towards mixed liquid crystal formation and vice versa. No such work seems to have been reported in binary mixtures where one component is a smectic liquid crystal and the other a non-mesomorphic one. Hence, it was thought worth while to explore the possibility of mixed liquid crystal formation in the smectic phase. Some twenty one systems of this type have been studied here, where ethyl p-azoxybenzoate - a prototype smectic liquid crystalline component - has been mixed with other non-mesomorphic Schiff's base compounds (Table - I).

Materials and Methods :

TABLE - I

Component A : Ethyl p-azoxybenzoate (a liquid crystal) mixed with

Component B :	M.P. °C	T.P. °C
1. Methyl p-chlorobenzylidene-p-aminobenzoate (Found : N, 4.954 %; $C_{15}H_{12}O_2NCl$ requires N, 5.118 %)	161.5	-
2. Methyl p-nitrobenzylidene-p-aminobenzoate (Found : N, 10.29 %; $C_{15}H_{12}O_4N_2$ requires N, 9.860 %)	213.0	-
3. Ethyl p-nitrobenzylidene-p-aminobenzoate (Found : N, 9.21 %; $C_{16}H_{14}O_4N_2$ requires N, 9.399 %)	180.0	-
4. p-Nitrobenzylidene-p-toluidine	124.0	-
5. p-Nitrobenzylidene-p-bromoaniline	163.0	-
6. p-Nitrobenzylidene-p-phenetidine	123.5	-
7. Methyl p-anisylidene-p-aminobenzoate (Found : N, 5.299 %; $C_{16}H_{15}O_3N$ requires N, 5.204 %)	132.5	-
8. Methyl p-dimethylaminobenzylidene-p-aminobenzoate (Found : N, 9.921 %; $C_{17}H_{18}O_2N_2$ requires N, 9.931 %)	163.5	-
9. p-Anisylidene-p-toluidine	93.0	-
10. p-Acetoxybenzylidene-p-bromoaniline	108.5	-
11. p-Chlorobenzylidene-p-phenetidine	123.0	-
12. p-Methylbenzylidene-p-toluidine	94.0	-

13.	p-Dimethylaminobenzylidene-p-chloroaniline (Found : N, 11.26 %; $C_{15}H_{15}N_2Cl$ requires N, 10.83 %)	152.0	-
14.	p-Chlorobenzylidene-p-dimethylaminoaniline	164.0	-
15.	p-Chlorobenzylidene-p-toluidine	128.0	-
16.	Ethyl p-chlorobenzylidene-p-aminobenzoate (Found : N, 4.620 %; $C_{16}H_{14}O_2NCl$ requires N, 4.868 %)	120.0	-
17.	Ethyl p-anisylidene-p-aminobenzoate (Found : N, 4.816 %; $C_{17}H_{17}O_3N$ requires N, 4.946 %)	80.0	-
18.	p-Anisylidene-p-bromoaniline	120.0	-
19.	p-Anisylidene-p-anisidine	148.0	-
20.	p-Anisylidene-p-chloroaniline	92.0	-
21.	p-Anisylidene-p-phenetidine	128.5	(122.0)

The precise measurements of various transition temperatures were made by the Leitz Ortholux polarizing microscope equipped with heating arrangement.

Results and Discussion :

Compounds 1 to 20 are non-mesomorphic and they do not exhibit liquid crystallinity either while heating or cooling and compound 21 is a monotropic nematic. When solid-mesomorphic and mesomorphic-isotropic transition temperatures of these binary mixtures are plotted against the mole per cent composition of the smectic compound, two types of curves

for smectic-isotropic transitions are obtained : (1) a usual curve where the transition lines are depressed regularly (Fig.1) and (2) a rising curve showing the maximum as observed in compounds 1 to 6 (Fig. 2 and 3). The maximum smectic-isotropic transition temperatures observed for compounds 1 to 6 are 127.0, 149.0, 139.5, 133.5, 138.0 and 147.5 ^{o}C respectively. In tables II and III are recorded the graphical observations of the study.

A smectic mesophase is a system of stratified structure in which rod-shaped molecules lie parallel in each stratum. Another substance dissolved in such a liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an unexpected manner. Unlike nematic mesophase, the smectic phase consists of strata of molecules and so some of the molecules of the compound dissolved in such a phase may occupy the place between smectic molecules in each stratum and the rest of the molecules may form a molecular stratum which may pack itself between the two strata of the smectic component, thus forming a homogeneous smectic melt. The tentative possible picture of such a melt is given in Fig. 4 where X represents the molecules of ethyl p-azoxybenzoate and Y represents the molecules of non-mesomorphic component. The degree of packing in this mode will depend upon molecular shape and size of the solute molecule and its functional groups. When the parallel molecules are arranged in layers where each molecule is perpendicular to the layer interfaces, (Fig.5) carrying terminal dipole moment parallel to major molecular axis as in p-substituted

nitro - or chloro- compounds, it becomes logical to assume that the terminal dipoles due to such groups may disturb the efficiency of the dipoles of the other groups of neighbouring smectic molecules, causing reduction in lateral intermolecular attractions and quite naturally we may expect, reduced smectic thermal stability of the mixture, compared to pure smectic component. However, in the course of this study, some compositions of binary mixtures comprising a nitro- compound and in a few cases a chloro- compound with ethyl p-azoxybenzoate, exhibit more smectic thermal stability than the pure smectic component, thus exhibiting a maximum when smectic-isotropic points are plotted against mole per cent of smectic component. It is rather difficult to explain such a behaviour. Gray and Byron[8] have explained the enhanced smectic thermal stability of 4-p-n-nonoxybenzylideneamino-4'-chlorobiphenyl in which terminal C-Cl dipole moment acts parallel to the major molecular axis, by assuming that the molecules are tilted at an angle to the layer interfaces; by tilting the molecules away from the perpendicular arrangement, the separation of the positive and negative charges of C-Cl dipoles do not necessarily increase but positive charge of one dipole can be brought nearer to the negative centre of the neighbouring dipole. At some suitable angle, the attractive forces will outweigh the repulsive forces and the net energy of attraction will enhance the lateral attractions and the smectic properties.

In the mixtures studied here, the smectic component has two dipole moments due to two terminal groups acting at an angle to main molecular axis, while one dipole moment due to

one of the two terminal groups of a non-mesomorphic component acts parallel and the other at an angle to the major molecular axis. Now, if we consider the molecular arrangement of mixture as shown in Fig. 4 and 5, to account for enhanced smectic properties of binary mixtures comprising non-mesomorphic compounds possessing terminal groups of high dipole moment (e.g. C-NO_2, C-Cl etc.), the molecular strata formed in the smectic melt would be tilted at an angle to the planes of the smectic strata where the net energy of attraction can become effective to enhance the lateral attractions and the smectic properties.

Aaron, Byron and Gray[8] have observed that in 4-p-x-benzylideneamino-4'-n-octoxybiphenyl when x represents -NO_2 or -Cl group, the nitro-substituted compound is thermally less stable than the corresponding chloro-compound, however, in the course of this study, when methyl p-chlorobenzylidene-p-aminobenzoate was mixed with ethyl p-azoxybenzoate, it gave a lower maximum of smectic-isotropic transition than the maximum obtained by mixing methyl p-nitrobenzylidene-p-aminobenzoate. These results suggest that from this limited data, it is hazardous to postulate the role of the terminally situated groups and their dipole moments on smectic characteristics of mixtures.

The study was carried out to deduce the slope of the transition curves in these binary mixtures similar to the study carried out be Dave and Dewar, and Dave and Lohar in nematic solutions. However, this is not possible as transition curves in these smectic mixtures are almost all curved and no order

TABLE - II

Solid to liquid or liquid crystal transition temperatures for the binary systems. The eutectic temperatures and melting points of pure components are direct experimental values: The other temperatures are read from phase-diagrams.

S.No.	Mole % of Ethyl p-azoxybenzoate.(A).											Eutectic	
	0	10	20	30	40	50	60	70	80	90	100	Mole %of(A)	Temp °C
1.	161.5	156.0	151.0	146.0	140.0	134.0	127.0	112.5	100.5	107.0	114.0	73.5	97.5
2.	211.5	206.5	201.0	194.5	187.5	179.0	169.0	155.0	135.5	101.5	114.0	89.5	100.5
3.	180.0	176.5	172.0	166.5	160.5	153.0	144.5	133.0	106.0	107.5	114.0	81.5	98.0
4.	124.0	119.0	114.0	109.0	104.0	99.0	91.0	81.0	94.0	105.0	114.0	67.5	76.5
5.	163.0	157.0	151.0	144.5	137.5	129.5	121.0	107.5	93.0	106.5	114.0	73.5	82.0
6.	123.5	119.5	116.0	112.5	108.5	100.5	88.5	82.0	95.5	106.5	114.0	67.0	77.5
7.	132.5	127.5	121.5	114.5	106.5	97.0	86.0	89.0	99.0	107.0	114.0	63.0	82.0
8.	163.5	158.5	153.5	148.5	143.0	136.5	127.5	113.0	101.0	107.5	114.0	75.5	98.0
9.	93.0	89.5	85.0	79.5	75.5	84.5	87.5	99.5	105.0	110.0	114.0	38.5	73.5
10.	108.5	104.0	100.0	96.0	92.5	88.5	90.5	99.5	104.5	109.0	114.0	58.0	85.5
11.	123.0	117.5	112.5	107.5	102.0	95.0	88.0	89.0	100.0	109.0	114.0	60.5	76.5
12.	94.0	88.5	83.0	78.0	77.5	87.5	94.0	99.5	104.0	107.5	114.0	37.0	74.0
13.	152.0	146.0	140.5	134.5	128.5	121.0	112.0	102.0	102.5	108.0	114.0	72.5	99.0

TABLE - II

14.	164.0	158.5	152.5	114.5	137.0	127.0	117.0	108.5	102.5	108.0	114.0	79.0	101.5
15.	128.0	121.5	115.0	109.0	102.5	96.0	89.5	91.0	98.0	107.0	114.0	64.5	86.5
16.	120.0	115.5	111.5	107.0	102.5	96.5	88.0	89.5	99.0	107.5	114.0	63.0	82.0
17.	80.0	76.5	74.0	77.5	81.0	85.5	91.0	93.5	101.5	108.5	114.0	18.5	73.5
18.	120.0	115.0	109.5	102.8	95.6	90.0	85.8	86.0	93.5	103.0	114.0	67.5	83.5
19.	148.0	142.5	137.0	131.5	125.4	118.2	110.2	102.0	101.0	107.2	114.0	74.5	97.5
20.	92.0	86.5	81.5	76.8	74.5	78.5	84.0	90.5	98.0	105.5	114.0	38.0	73.5
21.	128.5	123.0	107.8	112.5	106.0	99.5	92.4	93.0	99.5	106.5	114.0	64.0	89.0

TABLE - III

Smectic-isotropic transition temperatures for the binary systems. The values are read from the phase diagrams. The smectic-isotropic values for the pure compound is a direct experimental one. The values in the brackets show monotropy.

	Mole % of Ethyl p-azoxybenzoate										Triple point	
	40	50	60	70	75	80	85	90	95	100	Mole %of(A)	Temp. °c
1.	-	-	-	123.0	125.5	126.5	127.0	126.5	125.0	122.5	66.0	120.5
2.	-	-	-	(147.5)	148.5	148.5	147.0	143.0	137.5	122.5	73.5	148.5
3.	-	-	(126.0)	-	138.0	139.5	139.0	136.5	132.0	122.5	70.0	133.0
4.	-	111.0	123.0	130.0	132.0	133.0	133.5	132.0	129.5	122.5	45.5	101.5
5.	-	-	(118.5)	129.5	134.0	137.0	137.5	136.5	132.0	122.5	61.0	119.5
6.	125.0	134.5	143.0	147.0	147.0	146.0	143.5	139.5	133.0	122.5	29.0	112.5
7.	-	98.5	105.0	110.5	113.0	115.0	117.0	119.0	121.0	122.5	49.0	98.0
8.	-	-	(89.5)	100.0	104.5	109.0	113.0	116.5	119.5	122.5	74.0	103.5
9.	-	-	-	-	-	(104.0)	110.0	115.5	119.5	122.5	81.5	106.0
10.	-	-	-	-	(100.5)	109.0	114.0	117.5	120.0	122.5	75.5	102.0
11.	-	108.0	114.0	118.0	119.5	121.0	122.0	122.0	122.5	122.5	40.0	102.0
12.	-	-	-	-	-	(101.5)	106.5	112.0	117.5	122.5	84.0	105.5
13.	-	-	(97.0)	105.0	108.5	111.5	114.5	117.5	120.0	122.5	68.5	104.0
14.	-	-	-	111.0	113.5	115.5	117.5	119.5	121.0	122.5	68.0	110.0

TABLE - III

15.	-	-	93.0	104.0	108.5	112.5	116.0	118.5	121.0	122.5	58.0	91.0
16.	-	99.0	107.5	113.5	116.0	117.5	119.5	120.5	121.5	122.5	49.0	97.5
17.	(72.0)	(80.0)	(89.5)	(99.5)	104.0	108.5	112.5	116.0	119.5	122.5	62.0	91.5
18.	-	(88.5)	98.0	106.0	109.0	112.5	115.0	118.0	120.2	122.5	50.8	89.5
19.	-	-	-	(99.5)	102.5	105.8	109.5	103.5	118.0	122.5	71.5	100.5
20.	(72.0)	85.5	96.5	106.0	109.8	113.2	116.2	119.0	121.0	122.5	41.5	74.8
21.	-	-	(91.5)	101.0	105.0	108.6	112.5	116.0	119.0	122.5	60.5	92.0

for the tendency of the polar groups present in the non-mesomorphic component, can be derived.

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