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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 stereochemistry 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 possesses a 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

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 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

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

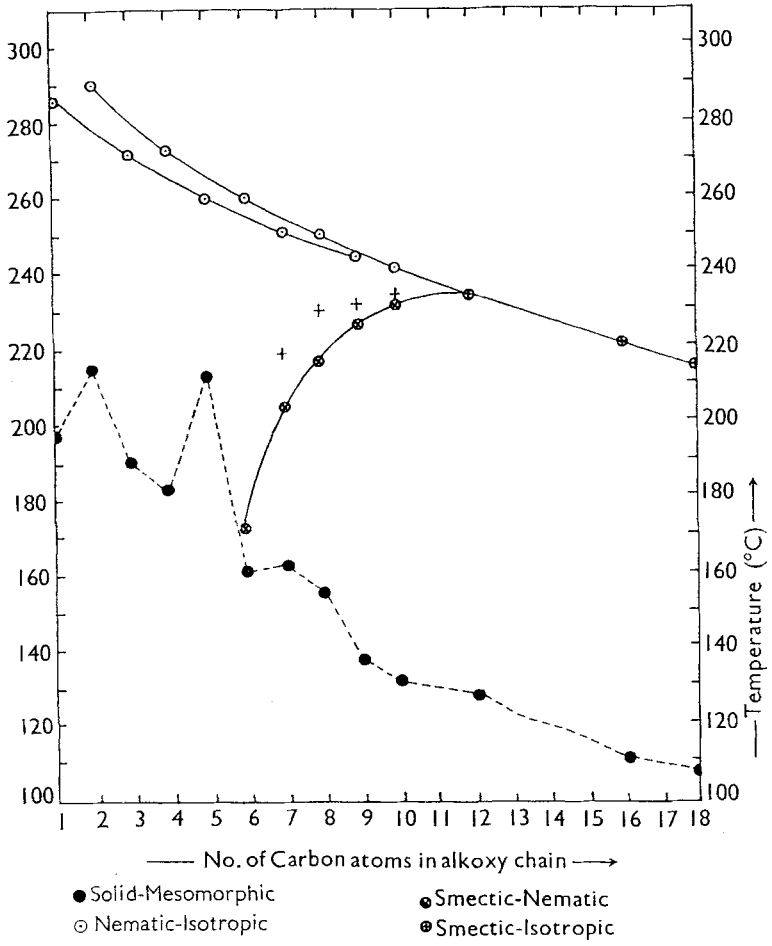


FIG. 1

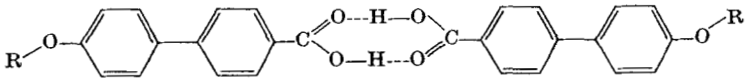
alkoxy chain and the other representing the ether with even number of carbon atoms in the alkoxy chain. The latter curve lies above the previous ones. Five smectic-nematic transition points

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.

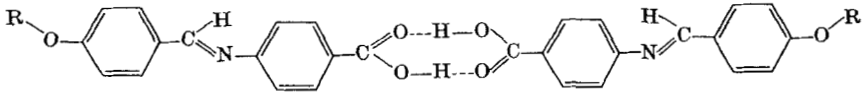
The following table summarizes the average thermal stabilities of smectic and nematic mesophases of the series, viz. *p*-n-alkoxybenzoic acids (A), *trans p*-n-alkoxycinnamic acids (B), 6-n-alkoxy-2-naphthoic acids (C), *p*-n-alkoxybenzylidene-*p*-aminobenzoic acids (I) and 4′-n-alkoxydiphenyl-4-carboxylic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

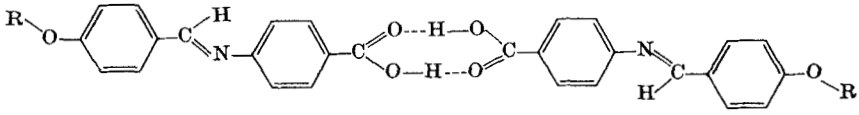
Comparison of the average thermal stabilities of these series shows that the average thermal stability of smectic and nematic mesophases of these series increases with the increase of double bonds but in the case of series I and D the former has less thermal stabilities than that of series D, in spite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



A—Strictly linear molecule.



or



B—Linear molecule but broader than A.

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

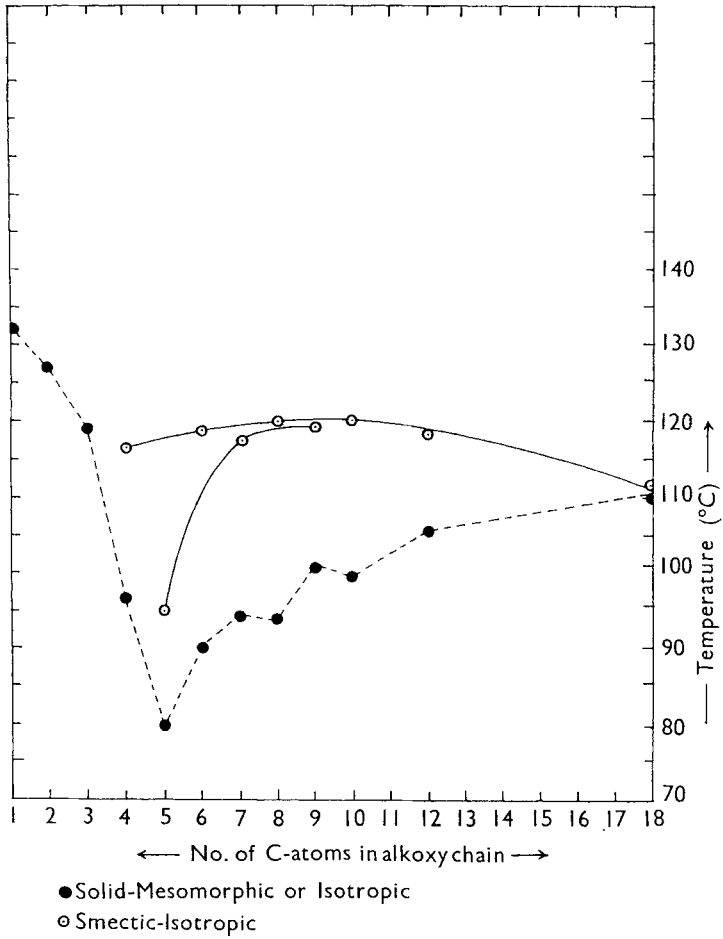


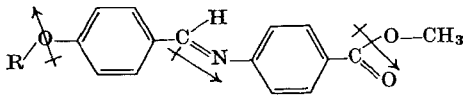
FIG. 2

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.

Methyl esters of *p*-n-alkoxybenzoic acids and *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 atoms 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*-aminobenzoate 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 temps. (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

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

axis, thus reinforcing the lateral cohesive forces. This is 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 1; the analytical data are given in Tables 3 and 4.

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