

Synthesis of new mesogens: 4(4'-*n*-alkoxy benzoyloxy)-phenyl-azo-4"-methyl benzenes

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Abstract. A homologous series with carboxy (–COO–) and azo (–N=N–), as central groups have been synthesised by treating 4-(4'-*n*-alkoxy benzoyl) chloride with 4-hydroxy phenylazo-4'-methyl benzenes. All the homologues of the series are mesomorphic in nature. The first eight members of the series are nematogenic and the remaining members exhibit smectic and nematic character with high melting behaviour and wide mesomorphic range. The usual odd-even effect does not predominantly appear in nematic isotropic transition curves but it appears to some extent in the first four homologues. Thermal stabilities are comparable with structurally similar known series.

Keywords. Liquid crystal; mesogen; mesomorphism; nematic; smectic.

1. Introduction

Work was planned with a view to synthesise new liquid crystalline material. A number of homologous series having ester and other linkages in their molecular geometry are reported. Some of them are purely smectogenic while others are polymesomorphic. The present new homologous series with –COO– and –N=N– central linkages offers good comparison in mesomorphic characteristics with other structurally related homologous series.

2. Experimental

2.1 Preparation

4-Hydroxy phenyl-azo-4'-methyl benzene was prepared by coupling *p*-toluidine and phenol by the usual method. The azo dye formed was filtered, washed with water, dried and crystallised in glacial acetic acid to constant melting point. Yield was about 60–70%.

n-Alkoxy benzoyl chlorides were condensed with the azo dye^{1,2}. Esters formed were purified in alcohol. Analytical data confirmed the structures (table 1). The transition temperatures are compiled in table 2.

2.2 Method of study

The transition temperatures (table 2) of the homologues were observed through a Laborlux polarising microscope provided with a Kofler heating stage.

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Table 1. Elemental analysis for 4(4'-*n*-alkoxy benzyloxy)-phenyl-azo-4''-methyl benzenes

Homologue	Molecular formula	Found (%)			Calculated (%)		
		C	H	N	C	H	N
Methyl	C ₂₁ H ₁₈ N ₂ O ₃	72.72	5.28	8.15	72.83	5.20	8.09
Ethyl	C ₂₂ H ₂₀ N ₂ O ₃	73.41	5.62	7.83	73.33	5.55	7.77
Propyl	C ₂₃ H ₂₂ N ₂ O ₃	73.71	5.79	7.40	73.79	5.88	7.48
Butyl	C ₂₄ H ₂₄ N ₂ O ₃	73.30	6.25	7.13	74.22	6.18	7.21
Pentyl	C ₂₅ H ₂₆ N ₂ O ₃	74.58	6.53	6.91	74.62	6.46	6.96
Hexyl	C ₂₆ H ₂₈ N ₂ O ₃	74.85	6.79	6.71	74.82	6.73	6.73
Heptyl	C ₂₇ H ₃₀ N ₂ O ₃	75.11	6.89	6.58	75.17	6.97	6.51
Octyl	C ₂₈ H ₃₂ N ₂ O ₃	76.15	7.43	6.17	75.50	7.20	6.30
Decyl	C ₃₀ H ₃₆ N ₂ O ₃	75.32	7.41	5.73	75.63	7.56	5.88
Dodecyl	C ₃₂ H ₄₀ N ₂ O ₃	76.98	8.13	5.74	76.87	8.00	5.60
Tetradecyl	C ₃₄ H ₄₄ N ₂ O ₃	77.37	8.39	5.35	77.27	8.33	5.30
Hexadecyl	C ₃₆ H ₄₈ N ₂ O ₃	77.72	8.79	5.12	77.69	8.63	5.03

¹H NMR 4(4'-*n*-propyloxy benzyloxy) phenyl-azo-4''-methyl benzenes: 6.9–8.184 ppm (*d*, *p*-substitution in the three benzene rings), 4.023 ppm (*t*, -OCH₂ of propyl), 2.442 ppm (*s*, CH₃-Ar), 1.844 ppm (*m*, CH₃-CH₂-CH₂), 1.072 ppm (*t*, CH₃-CH₂-CH₂)

Table 2. Transition temperatures of the homologous series 4(4'-*n*-alkoxy benzyloxy) phenyl-azo-4''-methyl benzenes

<i>n</i> -Alkyl group	Transition temperatures in °C		
	Smectic	Nematic	Isotropic
Methyl	–	150.0	270.0
Ethyl	–	151.0	279.0
Propyl	–	153.0	255.0
Butyl	–	129.0	250.0
Pentyl	–	123.0	235.0
Hexyl	–	105.0	224.0
Heptyl	81.0*	94.0	215.0
Octyl	86.0*	107.0	208.0
Decyl	89.0	96.0	193.0
Dodecyl	95.0	105.0	184.0
Tetradecyl	87.0	110.0	169.0
Hexadecyl	81.0	115.0	163.0

*Predicted monotropic smectic transition temperature from the graph

3. Results and discussion

Compounds belonging to the title homologous series are high melting mesogenic substances. Mesomorphism commences enantiotropically from the very first member of the series and continues up to the eighth homologue as a nematic mesophase. All the eight homologues show very sharp solid–nematic transitions at definite temperatures and smoothly transform into isotropic liquids at sharp transition temperatures. Transition temperatures are plotted against the number of carbon

atoms in the *n*-alkyl chains of alkoxy group and the various transition curves obtained are shown in figure 1. The nematic–isotropic transition curve shows smooth falling tendency as the series is ascended – a characteristic of a high melting series. Polymesomorphism commences from the decyl derivative of the series and continues up to the hexadecyl derivative. The smectic–nematic transition curve rises steeply as the series is ascended. Therefore the smectic phase range gets enlarged at the cost of the nematic mesophase which gets contracted as the series is ascended. The solid–mesomorphic curve shows a continuous overall falling tendency with an intermittent rise of a small range to the eighth and twelfth homologues. The mesomorphic range is high, which gradually decreases as the series is ascended. The usual odd–even effect does not predominantly appear in the nematic–isotropic transition curve but the first four homologues show this effect to some extent. Thereafter, the remaining homologues are of even number with the exception of the seventh. The smectic mesophase shows a focal conic fan-shaped structure which seems to belong to the A type. On extrapolation of the smectic–nematic transition curves to the left, the values of the probable monotropic transitions for the heptyl and octyl derivatives are 81°C and 86°C respectively. These values are not realisable due to the high crystallizing tendency of the mesomorphic melt on cooling of the nematic liquid.

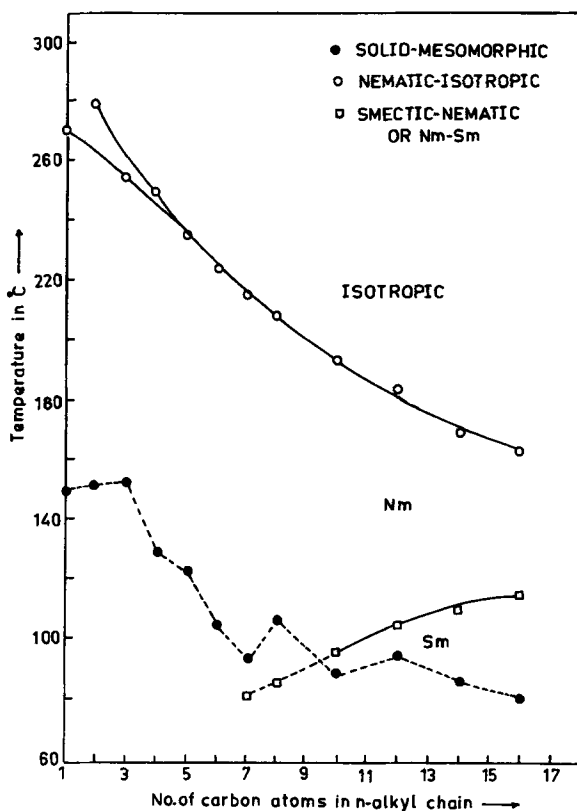


Figure 1. Phase transition diagram for 4(4'-*n*-alkoxy-benzoyloxy)-phenyl-azo-4''-methyl benzenes.

Table 3 shows the average thermal stabilities and the stage of commencement of the smectic phase for the title homologous series (1) and series selected for comparative study (2) and (3) (figure 2).

- (1) 4(4'-*n*-Alkoxy benzoyloxy) phenyl-azo-4''-methyl benzenes;
- (2) 4(4'-*n*-Alkoxy benzoyloxy) phenyl-azo-4''-isopropyl benzenes³;
- (3) 4(4'-*n*-Alkoxy benzoyloxy) benzylidene 4''-toluidines⁴.

4-Hydroxy phenyl-azo-4'-methyl benzene is a non-mesomorphic compound. However, a third benzene ring, with alkoxy terminal at the left, and an added carboxy group add to the overall length of the molecules and enhance lateral attractions as well as polarizability. This results in the molecules of the title series exhibiting mesomorphic characteristics.

The molecules of the first eight homologues of the series are capable of resisting the strong thermal vibrations at high temperatures that yield oriented anisotropic liquids. The molecules set themselves parallel to each other in a flowing condition giving rise to a threaded texture of nematic mesophase enantiotropically.

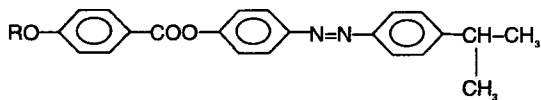
The π -electron density and the additional double bond at the central group $-N=N-$, coupled with the increase in the polarizability due to increase in length of the alkyl chain at the terminals of the linear molecules help the occurrence of the

Table 3. Average thermal stabilities ($^{\circ}\text{C}$)

Series	(1)	(2)	(3)
Nematic-isotropic	242.0 (C_1 - C_8)	189.7 (C_1 - C_4)	220.0 (C_1 - C_8)
Smectic-nematic	106.5 (C_{10} - C_{16})	99.2 (C_8 - C_{14})	154.2 (C_{12} - C_{18})
Commencement of smectic mesophase	C_{10}	C_8 (Monotropic)	C_7



(1) 4-(4'-*n*-alkoxy benzoyloxy) phenyl-azo-4''-methyl benzenes



(2) 4-(4'-*n*-alkoxy benzoyloxy) phenyl-azo-4''-isopropyl benzenes



(3) 4-(4'-*n*-alkoxy benzoyloxy) benzylidene-4''-toluidines

Figure 2. Structurally similar homologous series for comparison.

smectic mesophase. Hence an additional mesophase of the smectic variety appears with the nematic mesophase from the decyloxy to hexadecyloxy derivatives of the series within a definite range of temperatures.

The molecular geometries of the molecules of the title series (i.e. series 1) are compared to the series (2) and (3). The homologous series (1) resembles the series (2) in all respects but differs only in one aspect i.e., the terminal polarities of the $-\text{CH}_3$ and $-\text{C}(\text{CH}_3)\text{H}-\text{CH}_3$ groups. Likewise, the series (1) resembles series (3) in all respects except at the central bridging $-\text{N}=\text{N}-$ and $-\text{CH}=\text{N}-$ respectively.

Naturally the overall polarity and polarizability of the molecules belonging to different homologous series under comparison are comparable including the effect due to the non-coplanar nature of the molecules. Thus, most of the mesomorphic characteristics should also be comparable. The reasons for the variations that arise are obviously the different terminal groups at one end (series 1 to 2) and the different central bridges (series 1 and 3).

The nematic–isotropic as well as smectic–nematic thermal stability of series 2 is lower than the title series 1 under comparison. Methyl and isopropyl terminals are weakly dipolar in nature. Moreover, the isopropyl terminal unit broadens the molecules thereby decreasing intermolecular attraction as compared to the methyl unit. The overall length-to-breadth ratio and hence molecular polarizability and polarity are affected in such a manner that intermolecular attractions are diminished for homologues in series (2). Thus, long molecular axes may be forced apart by the isopropyl terminal unit reducing the intermolecular forces of attraction and consequently lowering the liquid crystal thermal stability i.e. the nematic–isotropic and smectic–nematic thermal stability of the liquid crystal.

While the nematic–isotropic thermal stability of the homologous series (3) is lower than that of the title series 1, the smectic–nematic thermal stability of series (3) is higher than that of the series 1. The molecules of series 3 contain one of the two central bridges as $-\text{CH}=\text{N}-$, while the $-\text{N}=\text{N}-$ central bridge is present in the title series 1 at the same place. The commonly present $-\text{COO}-$ central bridge in the molecules of series 1 and 3 causes⁵ bumping of the oxygen atom into the non-bonded sides of the adjacent hydrogens of the aromatic ring which in turn causes considerable strain on the molecule. Consequently, a twist occurs around the C–O bond forcing the benzene ring out of the plane of the molecule. Thus the co-planarity of the molecule is reduced to some extent making it thick. The extent of co-planarity is further affected by the presence of $-\text{N}=\text{N}-$ and $-\text{CH}=\text{N}-$ central bridges in series (1) and series (3) respectively. The central bridge $-\text{N}=\text{N}-$ certainly endows the molecules with co-planarity in the *trans* position while such behaviour is not exhibited to the same extent by $-\text{CH}=\text{N}-$ central bridge. On account of these differences, polarity and polarizability in combination with each other operate in such a way that a layered arrangement of molecules is strongly favoured amongst the molecules of the higher homologues of series 3 when compared to those of the series 1. Thus smectic–nematic thermal stability is higher in series 3. However, polarity and polarizability favour parallel orientation of molecules giving rise to a nematic mesophase. But the end-to-end attraction along the major axis of rotation are strengthened more in series 1 compared to series 3, giving rise to higher nematic–isotropic thermal stability in the title series. Late or early commencement of smectic mesophase in the series is related to the non-coplanarity of the molecules. Thus, the

commencement of the smectic phase is later at the decyloxy derivative stage when compared to series 2 and series 3.

4. Conclusions

New homologous mesogenic compounds have been synthesized. The series, with carboxy ($-\text{COO}-$) and azo ($-\text{N}=\text{N}-$) as central groups, have been synthesized by treating 4-(4'-*n*-alkoxybenzoyl) chloride with 4-hydroxy phenylazo-4'-methyl benzenes^{1,6}. The order of smectic and nematic group efficiencies is: $-\text{CH}_3 > -\text{C}(\text{CH}_3)_2-\text{CH}_3$. Similarly, the order of group efficiency for the smectic mesophase is: $-\text{CH}=\text{N}- > -\text{N}=\text{N}-$ and for the nematic mesophase is: $-\text{N}=\text{N}- > -\text{CH}=\text{N}-$.

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