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Azomesogens with polar chloro, nitro and phenolic –OH substituents[†]

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Two new mesogenic homologous series containing chloro, nitro and phenolic hydroxy groups were synthesised and their molecular structures characterised by a combination of element analysis and standard spectroscopic methods. The mesomorphic behaviour of the compounds of both series was investigated by polarising optical microscopy and, in some cases, differential scanning calorimetry. All the compounds of both the series exhibit an enantiotropic nematic mesophase. In series I higher members also exhibit an enantiotropic smectic A (SmA) mesophase, whereas in series II the enantiotropic SmA mesophase commences somewhat earlier for the middle members. The mesomorphic properties of both series are compared with each other and also with the properties of other structurally related series to evaluate the effects of different polar substituents on mesomorphism.

Keywords: azomesogen; polar substituent; smectic A phase

1. Introduction

Initially, it may be thought that anything that sticks out at the side of a molecule obviously disrupts molecular packing and therefore reduces liquid crystal phase stability. Indeed such disruption nearly always occurs through lateral substitution, but the situation is very subtle. In many cases this disruption to the molecular packing is particularly advantageous for the mesomorphic and physical properties required for applications, and some very interesting and useful materials have been generated by the appropriate use of lateral substitution. A wide range of different lateral substituents (e.g. –F, –Cl, –CN, $–NO_2$, $–CH_3$, $–CF_3$) has been incorporated into many different liquid crystal systems in many different environments (*1–5*). However, lateral hydroxy groups have been little exploited as it was reported that the phenolic "hydroxy" group might destroy mesomorphism, due to strong intermolecular hydrogen bonding (*6*). Schroeder and Schroeder (*7*) reported a few terminally hydroxy-substituted mesogens. Vora and Gupta (*8*) for the first time reported homologous series with terminal and lateral hydroxy groups. Subsequently, a few more mesogenic series with a lateral hydroxy group have been reported (*9–11*). Our group (*12–15*) has also reported a few mesogenic homologous series with an azo central linkage and lateral phenolic hydroxy groups. In continuation of our work on the synthesis and study of mesomorphic properties of compounds containing an azo central linkage, since azobenzenes are more stable compared to Schiff bases, and phenolic hydroxy substituent we have synthesised two new mesogenic homologous series of azobenzenes containing three rings in the main core and substituted by polar chloro and nitro groups along with phenolic –OH substituents (Scheme 1).

2. Experimental

4-Hydroxybenzoic acid, the appropriate *n*-alkyl halides, 2-chloro-4-nitroanile, 4-chloro-2-nitroanile, resorcinol, sodium nitrite, potassium hydroxide and thionyl chloride were used as received. Solvents were dried and distilled before use.

Characterisation

Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser, and the values obtained are in close agreement with those calculated. IR spectra were determined for KBr pellets using a Shimadzu IR-408 spectrophotometer. ^1H NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as internal reference standard. The chemical shifts are quoted in parts per million downfield from the reference; $CDCl_3$ was used as solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope equipped with a heating stage. The enthalpies of transitions, reported in $J\,g^{-1}$, were measured using differential scanning calorimetry (DSC) via a Mettler

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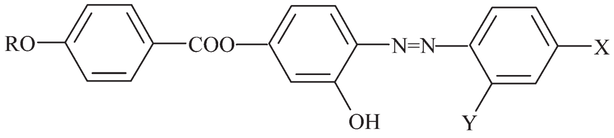


R = $-C_nH_{2n+1}$; n = 1 to 8, 10, 12, 14 & 16.
Series **I**: X = $-NO_2$ & Y = -Cl
Series **II**: X = -Cl & Y = $-NO_2$

Scheme 1. Structure of the new azobenzene derivatives.

TA-4000 system at a scanning rate of 5°C min^{-1}. The calorimeter was calibrated using pure indium as standard.

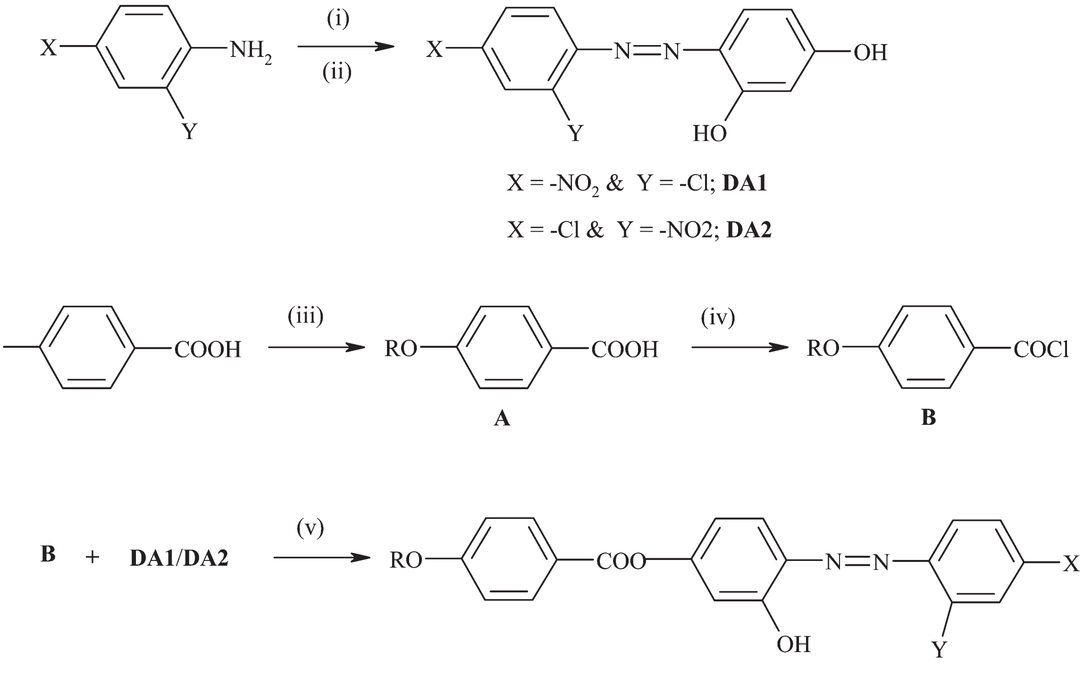
Synthesis

The synthetic routes to series I and series II compounds are illustrated in Scheme 2.

2-Chloro-4-nitro-2′,4′-dihydroxyazobenzene (**DA1**) and 4-chloro-2-nitro-2′,4′-dihydroxyazobenzene (**DA2**) were synthesised using conventional methods of diazotisation and coupling (*16*). 4-*n*-Alkoxybenzoic acids (**A**) and 4-*n*-alkoxybenzoyl chlorides (**B**) were synthesised by the modified method of Dave and Vora (*17*). The 24 monoesters of series I and series II were prepared by condensing equimolar quantities of 4-*n*-alkoxybenzyol chlorides with **DA1** and **DA2**, respectively, in dry pyridine and dichloromethane (*17*). All the monoesters were purified by column chromatography using silica gel (100–200 mesh size) and petroleum ether (60–80°C)–ethyl acetate mixture (96:4) as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallised from acetic acid until constant transition temperatures were obtained. The transition temperatures of series I and II compounds are recorded in Table 1. The elemental analysis of all the compounds was found to be satisfactory. IR and NMR spectral data for the *n*-octyloxy derivatives of both series are given below.

For series I, IR spectra showed –COO– stretching vibrations at 1737 cm^{-1}. Other signals observed were at 3300–3500 (–OH), 2961, 1606 (–N=N–), 1521, 1463, 1377, 1344, 1253, 1166, 1060, 844, 721 (C–Cl) cm^{-1}. ^1H NMR: δ 0.90 (t, 3H, $-CH_3$), 1.2–1.6 (m, 10H, 5 × $-CH_2-$), 1.83 (qunt., 2H, $-OCCH_2-$), 4.06 (t, 3H, $-OCH_2-$), 6.90–7.05 (m, 4H, ArH), 8.00–8.30 (m, 6H, ArH), 13.1 (s, 1H, –OH).

For series II, IR spectra showed –COO– stretching vibrations at 1737 cm^{-1}. Other signals observed were at 3300–3500 (–OH), 2923, 1604 (–N=N–),



R = $-C_nH_{2n+1}$; n = 1-8, 10, 12, 14 & 16
X = $-NO_2$ & Y = -Cl; Series **I**
X = -Cl & Y = $-NO_2$; Series **II**

Reagents and conditions: (i) $NaNO_2$, HCl, 0-5 °C (ii) Resorcinol in NaOH, 0-5 °C, HCl
(iii) RBr, KOH, Ethanol (iv) $SoCl_2$ in Excess (v) Dry Pyridine, HCl, 5-10 °C

Scheme 2. Synthetic routes to series I and series II compounds.

Table 1. Transition temperatures (°C) of the series I and II compounds.

Compound	*n*	Cr		SmA		N		I
Series I								
1	1	•	212	–	–	•	296	•
2	2	•	172	–	–	•	272	•
3	3	•	152	–	–	•	260	•
4	4	•	133	–	–	•	258	•
5	5	•	105	–	–	•	257	•
6	6	•	100	–	–	•	251	•
7	7	•	95	•	162	•	240	•
8	8	•	75	•	165	•	221	•
9	10	•	76	•	175	•	209	•
10	12	•	84	•	177	•	206	•
11	14	•	90	•	179	•	204	•
12	16	•	85	•	180	•	195	•
Series II								
13	1	•	164	–	–	•	262	•
14	2	•	135	–	–	•	252	•
15	3	•	125	–	–	•	225	•
16	4	•	105	–	–	•	211	•
17	5	•	103	–	–	•	196	•
18	6	•	95	–	–	•	182	•
19	7	•	93	–	–	•	175	•
20	8	•	89	–	–	•	173	•
21	10	•	94	–	–	•	168	•
22	12	•	91	–	–	•	147	•
23	14	•	78	•	90	•	140	•
24	16	•	86	•	95	•	138	•

1527, 1463, 1377, 1338, 1249, 1184, 1058, 859, 721 (C–Cl) cm^{-1}. ^{1}H NMR: δ 0.89 (t, 3H, –CH_3), 1.2–1.6 (m, 10H, 5 × –CH_2–), 1.83 (qunt., 2H, –$OCCH_2$–), 4.05 (t, 3H, –OCH_2–), 6.93–7.02 (m, 4H, ArH), 7.70–8.20 (m, 6H, ArH), 12.6 (s, 1H, –OH).

3. Results and discussion

Optical microscopic studies

As a preliminary investigation, the mesophases exhibited by compounds of series I and II were examined using a polarising optical microscope. Thin films of the samples were obtained by sandwiching them between a glass slide and cover slip. All of the series I and II compounds synthesised were found to exhibit mesomorphism.

On cooling from the isotropic liquid, methoxy to *n*-hexadecyloxy derivatives of series I exhibited a threaded/marble texture characteristic of a nematic mesophase, which on further cooling ($n \geqslant 7$) transformed into the focal conic texture of a smectic A (SmA) mesophase. In series II, on cooling from the isotropic liquid, all derivatives synthesised exhibited the threaded/marble texture characteristic of a nematic mesophase, which on further cooling ($n \geqslant 14$) transformed into the focal conic texture of a SmA mesophase.

DSC studies

As representative cases, the phase transition enthalpies were measured for the *n*-butyloxy derivative of series I as well as the *n*-decyloxy and *n*-dodecyloxy derivatives of series II by DSC. The results are recorded in Table 2. Enthalpy changes for the various transitions agree well with existing literature values for similar compounds (*18*).

Table 2. DSC data for series I and II compounds.

Series	*n*	Transition	Peak temperature/°C	Δ*H*	Δ*S*
I	4	Cr$_1$–Cr	110.1	20.48	0.0535
		Cr–N	133.0	70.77	0.1741
		N–I	261.1	4.57	0.0086
II	10	Cr–N	93.4	66.56	0.1817
		N–I	168.4	0.77	0.0017
	12	Cr–N	91.6	71.57	0.1963
		N–I	144.4	1.31	0.0031

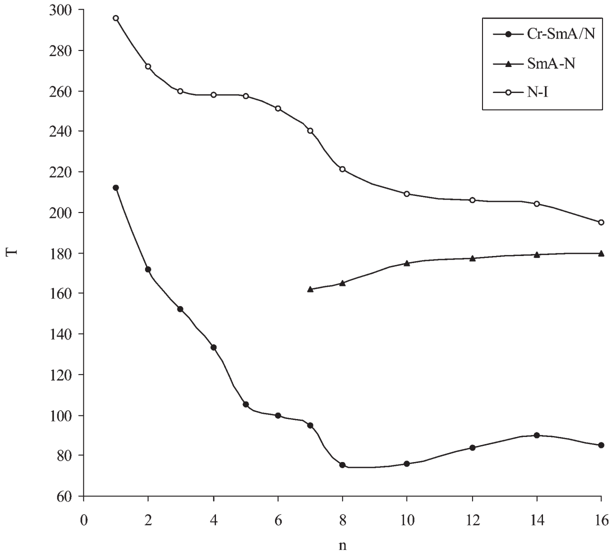


Figure 1. The phase behaviour of series I compounds.

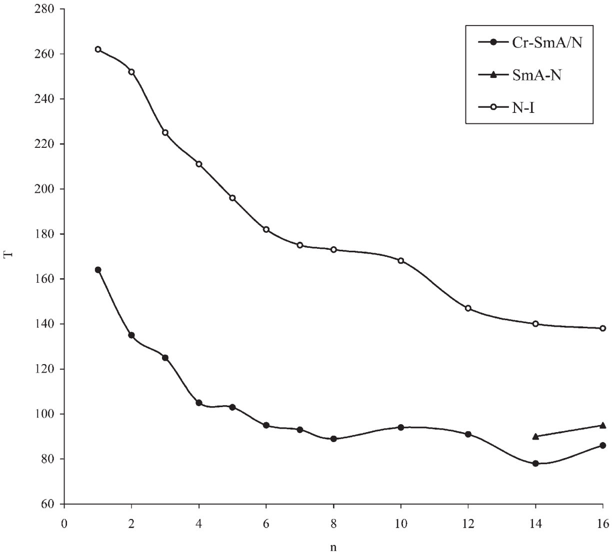


Figure 2. The phase behaviour of series II compounds.

Phase behaviour

Series I: 2-chloro-4-nitro-2′-hydroxy-4′-(4″-n-alkoxybenzoyloxy)azobenzenes.

Twelve compounds of series I were synthesised and their mesogenic properties evaluated. All the members synthesised exhibit an enantiotropic nematic mesophase. A SmA mesophase appears from the *n*-heptyloxy derivative as an enantiotropic phase and remains in the series up to the *n*-hexadecyloxy derivative. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Figure 1) shows a smooth falling tendency for nematic–isotropic (N–I) transition temperatures. SmA–N transition temperatures exhibit a rising tendency as the series is ascended.

Series II: 4-chloro-2-nitro-2′-hydroxy-4′-(4″-n-alkoxybenzoyloxy)azobenzenes.

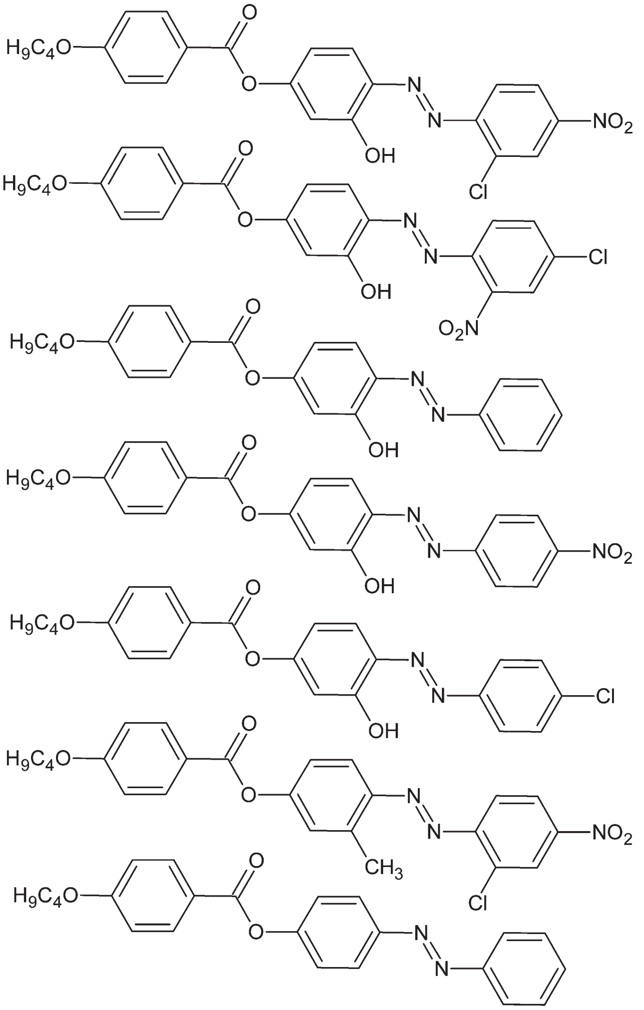
All twelve members of series II synthesised exhibit an enantiotropic nematic mesophase. *n*-Tetradecyloxy and *n*-hexadecyloxy derivatives also exhibit an enantiotropic SmA mesophase. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Figure 2) shows a smooth falling tendency for N–I transition temperatures. SmA–N transition temperatures exhibit a rising tendency as the series is ascended.

Mesogenic properties and molecular constitution

It is well known that thermotropic liquid crystals are highly sensitive to their molecular constitution. It is of prime importance, from the chemist's point of view, to determine the effects of alterations in the molecular core on the mesogenic properties of a compound. The thermal stability and mesophase length as a measure of mesomorphism can be correlated with the molecular constitution of the compounds.

Table 3 summarises the mesophase range (width of mesophase), thermal stability (N–I transition temperature) and molecular structure of the *n*-hexyloxy derivative of present series I and II (compounds **4** and **16**) and structurally related compounds **A** (*14*), **B** (*15*), **C** (*14*), **D** (*19*) and **E** (*20*). The nematic mesophase length and thermal stabilities of the series I compound are higher by 19°C and 47°C, respectively, than those of the series II equivalent. Also, the smectic mesophase commences from the *n*-heptyloxy derivative in series I, whereas it commences later from the *n*-tetradecyloxy derivative in series II. The only difference in molecular geometry is in the position of the polar nitro and chloro groups on the terminal benzene ring. In series I, the nitro group is *para* and chloro group is in the *ortho* position in relation to the azo central linkage, whereas in series II the nitro group is *ortho* and chloro group is in the *para* position in relation to the azo central linkage. Thus, compared with the molecules of series I, the molecules of series II have increased breadth due to the bulky lateral nitro group on the terminal benzene ring. Gray (*21*) has explained that an increase in the breadth of the molecules reduces both nematic and smectic mesophase stability. It seems that the lateral nitro group not only increases the breadth of the molecules of series II but also increases the acoplanarity in the system due to

Table 3. Comparison of mesophase range (°C), thermal stability (°C) and molecular structure of compounds **4**, **16**, **A**, **B**, **C**, **D** and **E**.



Compound **4**

Compound **16**

Compound **A**

Compound **B**

Compound **C**

Compound **D**

Compound **E**

Compound	Cr		N		I	Mesophase range	Commencement of smectic phase
4	•	133	•	258	•	125	C_7
16	•	105	•	211	•	106	C_{14}
A	•	113	•	165	•	52	C_{16}
B	•	81	•	221	•	140	C_{10}
C	•	125	•	228	•	103	–
D	•	116	•	175.5	•	59.5	C_{16}
E	•	146	•	165	•	19	–

steric interactions. Both these factors would decrease the nematic mesophase range and thermal stabilities for compound **16** as well as smectogenic tendencies of series II reported in the present investigation.

Reference to Table 3 indicates that the nematic mesophase length and N–I transition temperatures of both the present compounds, **4** and **16**, are higher than those of compound **A**. This is understandable as the presence of polar nitro and chloro substituents increases the polarisability of the molecule of compounds **4** and **16** without much increase in the molecular breadth as compared to compound **A**.

In the case of compound **4**, the width of the nematic phase is lower by 15°C than that of compound **B**. Gray (*21*) has explained that a compound that requires more thermal energy to disorganise its parallel molecular arrangement in the nematic phase is thermally more stable. As can be seen in Table 3, more thermal energy has to be supplied to disorganise the parallel molecular arrangement of the nematic phase of compound **4**, evidenced by the fact that the N–I transition temperature is higher by 37°C than that for the compound **B**. The higher N–I transition temperatures of compound **4** may be due to the polar nature of the lateral chloro group, which increases the overall polarisability of the molecules of compound **4** without much increase in the breadth of the molecule as compared to compound **B**. The range and thermal stability of the mesophase is a more important factor in relating mesomorphic behaviour to chemical constitution since the chemical grouping gives rise to intermolecular attractions, which in turn determine the mesophase range and thermal stability. One should remember too that the length of the mesophase is determined partly by the Cr–N transition temperatures.

Reference to table 3 also indicates that the width of the nematic phase of compound **16** is higher by 3°C than that of compound **C**, whereas the N–I transition temperature is lower by 17°C than that for the compound **C**. As discussed earlier, this is probably due to the increase in the breadth of the molecule of compound **16** as compared to compound **C** due to presence of lateral bulky nitro group in compound **16**.

Reference to Table 3 indicates that the mesophase range and N–I transition temperature of compound **4** is higher by 65.5°C and 82.5°C, respectively, than those of compound **D**. Molecules of compound **4** and **D** differ only in the lateral substituent at the central benzene ring. Compound **4** has a lateral phenolic –OH group, whereas compound **D** has a lateral methyl group at that position. The latter increases the breadth of the molecules leading to a decrease in mesophase thermal stabilities. In compound **4** the phenolic –OH group is present *ortho* to the azo central linkage, leading to intramolecular hydrogen bonding and higher nematic mesophase length as well as thermal stabilities. This is also reflected in the comparison of compound **4** and compound **E**, where the mesophase range and N–I transition temperatures of compound **4** is higher by 106°C and 93°C, respectively, as the molecule of compound **4** contains not only the phenolic –OH substituent but also the polar nitro and chloro substituents. These results agree well with those reported previously by Vora and Gupta (*8*) and our group (*12, 13*), which showed that mesogenic homologous series with a lateral phenolic –OH group exhibits liquid crystalline properties with higher thermal stabilities compared to the non-hydroxy analogues.

4. Conclusion

In this paper we have reported the synthesis and characterisation of two new homologous series of azomesogens containing polar chloro, nitro and phenolic –OH substituents. The study indicated that the lateral polar chloro group stabilises the mesophase, as it does not increase the breadth of the molecule much for series I, whereas lateral polar nitro group adversely affects mesophase thermal stability due to an increase in the breadth of the molecule of series II. The study also indicated that the compounds of series I and II exhibit a nematic phase as well as a smectic A phase with good mesophase range and higher thermal stabilities due to the presence of polar nitro and chloro groups as compared to structurally related compounds without polar nitro and chloro groups. Due to the strong intramolecular hydrogen bonding the compounds of series I and II exhibit higher mesophase length as well as thermal stabilities compared to their non-hydroxy analogues.

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