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Two homologous series are synthesized by fixing a rigid 4-methyl phenyl azo group to resorcinol moiety. In series I one phenolic -OH group is alkylated whereas, in series II both the phenolic -OH groups are alkylated. Monoethers of series I having free lateral hydroxy group due to strong hydrogen bonding, exhibit nematic mesophases whereas, diethers of series II are non-mesogenic.

Keywords: azobenzene derivatives; nematic mesophase

INTRODUCTION

In general but not exclusively, the rod-like or lath like molecular shape is an important factor for displaying mesomorphic properties. The presence of a rigid substituent usually reduces or destroys the temperature range of the liquid crystalline phase^[1-3]. Usually a lateral substituents introduced into mesogen molecules depress the thermal stability of the mesophases. This effect is related to the overall anisotropic broadening of the molecule and its consequence on the cooperative packing needed in the mesophase^[4]. This depression depends on several parameters such as the phase type, the substituent type, and the substituent position within the core.

Number of mesogens with various substituents are reported in the literature^[5] but the mesomorphic compounds incorporating a phenolic or a primary amino group are rare^[6-8]. Schroeder and Schroeder^[9] reported a few such mesogenic

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compounds. Mesogenic compounds with terminal alcoholic^[10] or amino groups^[11] are also reported in the literature. Vora and Gupta^[12] for the first time reported two extensive homologous series containing terminal and lateral phenolic groups. Subsequently few more mesogenic series with lateral phenolic groups have been reported^[13–16]. Mesogenic Schiff's base compounds with intramolecularly hydrogen bonded phenolic groups are also found in the literature^[17–20]. Recently Vora and Prajapati^[21] reported a first extensive mesogenic *homologous series of Schiff's base esters with a lateral thiol group*. Gray^[22] has explained that the rarity of such mesogenic compounds may be due to intermolecular hydrogen bonding and broadening of the molecules. In this paper, we first present the synthesis of mesogenic homologous series-I containing only two-ring in the main core with a lateral phenolic group.

Mesogens with lateral alkoxy substituent are of interest because they deviate from the classical rod like shape^[15,23]. Bayle *et. al.*^[16,24] reported that in a four-ring mesogenic core, it was possible to introduce two lateral alkoxy chains on the same side of an inner ring without depleting the liquid crystal properties. In this paper we present the synthesis of homologous series-II with lateral alkoxy chain in order to study whether it is possible to introduce one lateral alkoxy chain in a short two-ring system without depleting the mesomorphic properties.

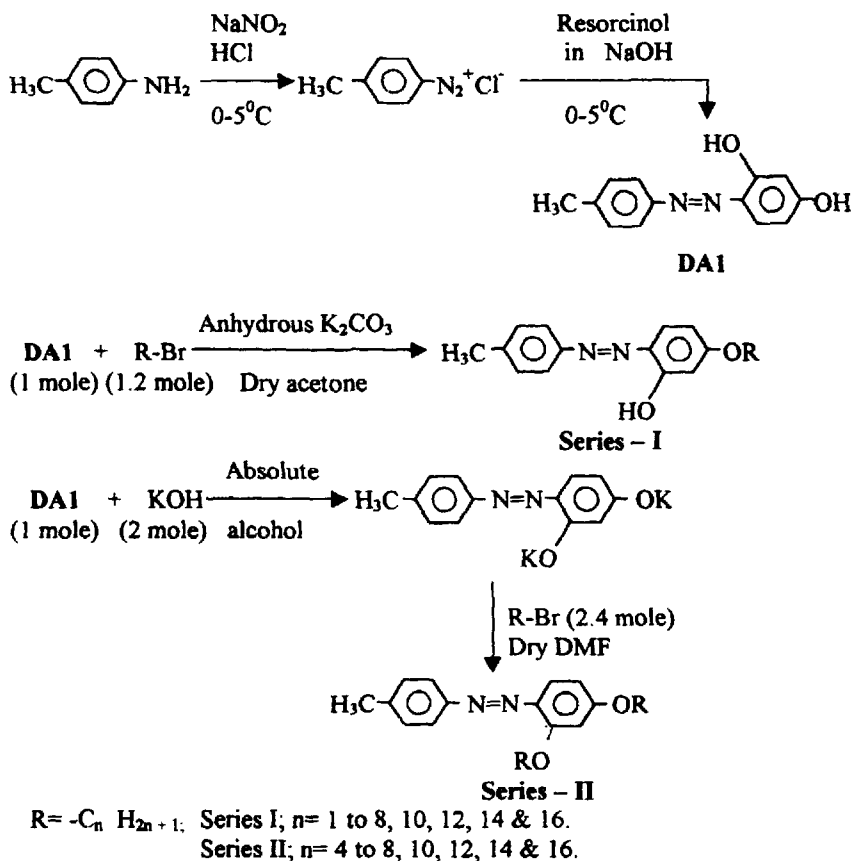
EXPERIMENTAL

Characterization

Elemental analysis were performed on a Coleman carbon-hydrogen analyser and the values obtained are in close agreement with those calculated. IR spectra were determined via KBr pellets, using a Shimadzu IR-408 spectrophotometer. ¹HNMR spectra were obtained with a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. CDCl₃ was used as a solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. The enthalpies of transitions reported as J/g, were determined from thermograms obtained on a Mettler TA-4000 system, adopting a scanning rate of 5°C/min.

Synthesis

The synthetic route to series I and II is illustrated in Scheme 1.



SCHEME 1 Synthetic route to Series I and II

Anhydrous solvents were prepared from commercial solvents following the standard procedures. All the solid starting materials were obtained from Alderich and Merck Ltd.. 4-Methyl 2',4'-di-hydroxy azobenzene (DA1) was synthesized by using conventional method of diazotization and coupling^[25].

Synthesis of series I compounds

A mixture of DA1 (206 mg, 0.8 mmol), appropriate n-alkylhalide (0.96 mmol), anhydrous potassium carbonate (166 mg, 1.2 mmol) and dry acetone (20 ml) was heated under reflux for 8h. The whole mass was then added to the water. The

product monoether was filtered off and was crystallised repeatedly from ethanol till constant transition temperatures were obtained.

Synthesis of series II compounds

The procedure describe above failed in dialkylation of DA1. A modified method described below was used for dialkylation of DA1 to synthesize compounds of series II.

DA1 (0.8 mmol) and potassium hydroxide (90 mg, 1.6 mmol) were taken in 20 ml absolute alcohol and heated under reflux for 1h. The dry potassium salt was obtained by distilling off ethanol from the mixture. To the dipotassium salt contained in flask, was added, appropriate *n*-alkylhalide (1.92 mmol) and dry dimethylformamide (20 ml). The mixture was heated under reflux for 12h. The mixture was poured into water and the product was then extracted with ether. The ether extract was washed successively with water (2x30 ml), 10% aqueous sodium hydroxide (3x50 ml), water (3x30 ml); it was then dried (Na₂SO₄). The solid obtained on removal of ether was crystallised repeatedly from methanol till constant melting point was obtained.

The chemical structures of all the compounds were confirmed by using a combination of elemental analysis, IR and ¹HNMR spectroscopy. The characterization of *n*-butyl derivative of both the series I and II are given below.

Elemental data

Series I: Found, C71.62, H7.32, N9.78%. C₁₇H₂₀N₂O₂ requires, C71.83, H7.04, N9.86%.

Series II: Found, C74.24, H8.15, N8.55%. C₂₁H₂₈N₂O₂ requires, C74.12, H8.23, N8.23%.

IR spectra

Series I: 3600–3200 (–OH), 2900, 1610 (–N=N–), 1500, 1400, 1280, 1240, 1200, 1030, 815, 720 cm^{–1}.

Series II: Series II: 2950, 1610 (–N=N–), 1500, 1400, 1380, 1285, 1240, 1195, 1045, 810, 715 cm^{–1}.

¹HNMR spectra

Series I: δ 0.95 (t, 3H, -CH₃), 1.5–1.8 (m, 4H, 2 \times -CH₂) 2.4 (s, 3H, ArCH₃), 4.0 (t, 2H, -OCH₂-) 6.4–6.6 (m, 3H, ArH), 7.0 (d, 2H, ArH) 7.3 (d, 2H, ArH), 13.5 (s, 1H, OH)

Series II: δ 0.95 (t, 6H, 2 \times -CH₃), 1.3–1.8 (m, 8H, 4 \times -CH₂-), 2.35 (s, 3H, ArCH₃), 3.8–4.1 (m, 4H, 2 \times -OCH₂-), 6.4–6.6 (m, 3H, ArH), 7.0 (d, 2H, ArH), 7.2 (d, 2H, ArH).

RESULTS AND DISCUSSION

The transition temperatures and the melting points for compounds of series I and II are recorded in table I. The associated enthalpies for few compounds of the series I are summarized in table II.

TABLE I Transition temperatures and melting point for series I and II compounds

| Compound No. | <i>n</i> = Series I | Transition temperatures and melting point(°C). | |
|--------------|----------------------|--|----------|
| | | <i>N</i> | <i>I</i> |
| 1 | 1 | – | 147.0 |
| 2 | 2 | – | 143.0 |
| 3 | 3 | (70.0) | 100.0 |
| 4 | 4 | 86.0 | 90.0 |
| 5 | 5 | 66.0 | 75.0 |
| 6 | 6 | 85.0 | 89.0 |
| 7 | 7 | 64.0 | 89.0 |
| 8 | 8 | 71.0 | 88.0 |
| 9 | 10 | 70.0 | 86.0 |
| 10 | 12 | 65.0 | 84.0 |
| 11 | 14 | 64.0 | 81.0 |
| 12 | 16 | 72.0 | 80.0 |
| Compound No. | <i>n</i> = Series II | Melting point. <i>I</i> | |
| 13 | 4 | 53.0 | |
| 14 | 5 | 49.0 | |
| 15 | 6 | 45.0 | |
| 16 | 7 | 56.0 | |
| 17 | 8 | 59.5 | |
| 18 | 10 | 43.5 | |
| 19 | 12 | 47.5 | |
| 20 | 14 | 54.0 | |
| 21 | 16 | 49.0 | |

() Monotropic transition. N= nematic phase; I= isotropic phase; n= number of carbon atoms in alkoxy chain.

TABLE II DSC data for series I compounds

| Sr. No. | Compound No. | Transition | $\Delta H/Jg^{-1}$ | $\Delta S/Jg^{-1}K^{-1}$ |
|---------|--------------|------------|--------------------|--------------------------|
| 1 | 4 | Cr-N | 15.51 | 0.0432 |
| | | N-I | 0.96 | 0.0026 |
| 2 | 8 | Cr-N | 16.43 | 0.0478 |
| | | N-I | 1.24 | 0.0034 |
| 3 | 10 | Cr-N | 29.75 | 0.0880 |
| | | N-I | 1.62 | 0.0045 |
| 4 | 12 | Cr-N | 22.34 | 0.0648 |
| | | N-I | 1.87 | 0.0053 |

Cr= crystalline phase; N= nematic phase; I= isotropic phase.

Series-I

4-Methyl (2'-hydroxy, 4'-n-alkoxy) azobenzenes.

This series is purely nematogenic. The first two derivatives of the series are non-mesogenic. n-Propyloxy derivative exhibits monotropic nematic phase. Higher members exhibit an enantiotropic nematic phase.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (figure 1), shows a steady fall in the nematic- isotropic transition temperature, except odd derivatives which shows rising tendency, and exhibits a marked odd-even effect.

Series II

4-Methyl (2',4'-di-n-alkoxy) azobenzenes.

All the derivatives of the series are non-mesogenic. Even the supercooling of the compounds do not show the emergence of a monotropic mesophase in any of the compounds.

Compounds of series I have clearing temperatures somewhat higher than the corresponding compounds (4,4'-Bis-n-alkyl and 4-n-alkyl-4'-n-alkoxy azobenzenes) without an o-hydroxyl group^[5]. There are compounds in which the lateral substituents are shielded, so that they are less effective in broadening of the molecule^[4]. The compounds of series I may give rise to shielding effects due to intramolecular association^[18,19,26] and hence the polarizability along the long axis of molecule will be larger in such compounds than that of unsubstituted analogs. This will result into higher clearing temperatures than the corresponding compound without an o-hydroxyl group.

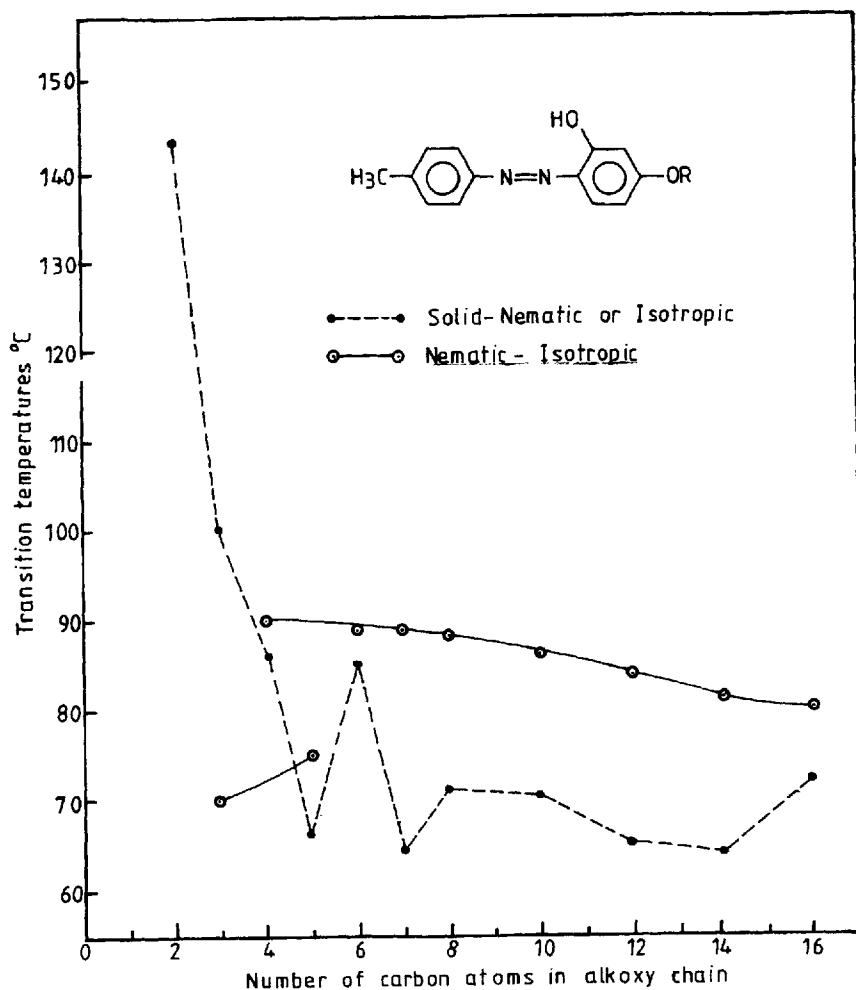


FIGURE 1 The phase behavior of the present series I

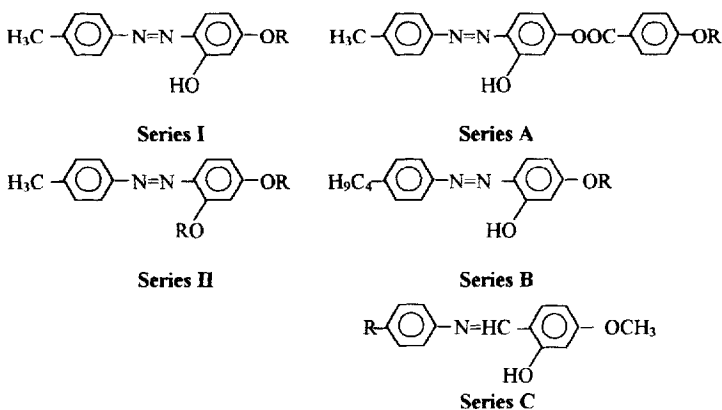
Table III summarizes the average nematic thermal stabilities and comparative geometry of the present series I and II and the structurally related series A^[27], B^[26] and C^[18].

The average nematic thermal stabilities of series I are much lower than those of series A. This can be attributed to the shorter length and lower polarizability of series I molecules due to presence of only two phenyl ring and one central linkage.

TABLE III Average thermal stabilities

| Series | I | A | B | II | C |
|---------------------------------------|-------|--------|-------|----|---|
| N-I(C ₃ -C ₁₀) | 83.85 | 229.86 | 77.57 | – | 71.73 (C ₃ -C ₇ , C ₁₂) |

N= nematic phase; I= isotropic phase; C₃-C₁₀= n-propyloxy derivative to n-decyloxy derivative; C₃-C₇=n-propyloxy derivative to n-heptyloxy derivative, C₁₂= n-dodecyloxy derivative.



Comparative geometry of Series I, II, A, B and C.

Reference to table III indicates that the average nematic thermal stability of series I is slightly more than that of series B. This is understandable as there is little difference in the geometry of the two series, the terminal group being changed from $-\text{CH}_3$ to $\text{n-C}_4\text{H}_9$.

The present series I exhibit nematic mesophase whereas series II is non-mesogenic. The molecules of series I and II have only two phenyl group but the presence of lateral n-alkoxy substituent in series II disturbs the close packing of the molecules in such a short two phenyl ring system leading to non-mesogenic property.

Table III shows that the average nematic thermal stability of series I is higher than that of series C. Molecules of series I and C differ in central linkage and terminal groups. Series I has an azo central linkage whereas series C has an azomethine central linkage. Molecules of series I also have n-alkoxy group at the *meta* position of the lateral hydroxy group and methyl group on the other benzene nucleus as a terminal substituents whereas series C has methoxy group and n-alkyl group in place of n-alkoxy group and methyl group of series I, respectively. The $-\text{N}=\text{N}-$ central linkage is more coplanar than $-\text{CH}=\text{N}-$ central linkage also the terminal n-alkoxy group increases the overall polarizability of the molecules of series I compare to series C therefore the nematic thermal stability of series I should be little higher than those of series C, which is the case.

CONCLUSION

As Schiff's base are unstable compared with azobenzenes, in this paper, we have presented the synthesis and mesomorphic properties of two new series of azobenzenes containing two rings in the main core, and a lateral hydroxy or lateral n-alkoxy group.

The nematic thermal stability of the present series I is higher than the corresponding unsubstituted azo compounds as well as the structurally related intramolecularly hydrogen bonded Schiff's bases. Due to strong intramolecular hydrogen bonding the short two phenyl ring system with lateral hydroxy group (series I) exhibit nematic mesomorphism whereas it is difficult to introduce bulkier lateral n-alkoxy group in such a short two phenyl ring system without depleting the liquid crystal properties and hence series II was found to be non-mesogenic.

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