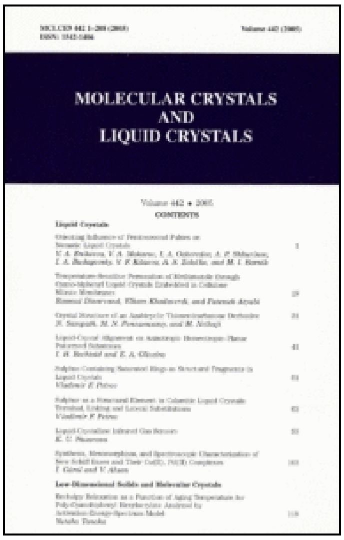

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# Effects of Different Terminal Substituents on the Mesomorphic Behavior of Some Azo-Schiff Base and Azo-Ester-Based Liquid Crystals

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# Effects of Different Terminal Substituents on the Mesomorphic Behavior of Some Azo-Schiff Base and Azo-Ester-Based Liquid Crystals

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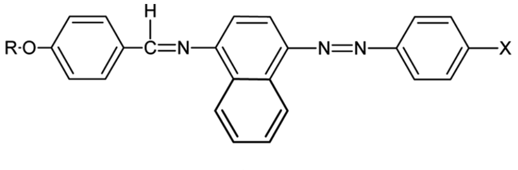
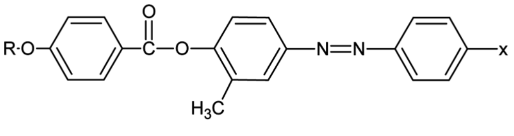
*In order to investigate the influence of the terminal substitution on mesomorphism, two new series of azo-Schiff base and azo-ester liquid crystals having the following structures have been synthesized. All the compounds possess mesomorphic properties. In series A compounds $A_1$ and $A_3$ exhibit only a nematic mesophase, whereas compounds $A_2$, $A_4$, $A_5$, $A_6$, $A_7$, $A_8$, $A_9$, and $A_{10}$ exhibit a smectic as well as a nematic phase. In series B compounds $B_1$ to $B_9$ exhibit only a nematic mesophase, and compounds $B_{10}$ and $B_{11}$ exhibit a smectic as well as a nematic phase, but compound $B_{12}$ exhibits only a smectic phase. All these compounds were characterized by elemental analyses and spectroscopic techniques (Fourier transform infrared [FTIR], $^1$H nuclear magnetic resonance [NMR], and mass spectroscopy). Their mesomorphic properties were measured by optical polarized light microscopy and differential scanning calorimetry (DSC).*



Series A



Series B

Series A: R = $C_8H_{17}$ and $C_{16}H_{33}$ where X= -H, -$CH_3$, -$OCH_3$, -Cl, -Br

Series B: R = $C_8H_{17}$ and $C_{16}H_{33}$, where X= -H, -$CH_3$, -$OCH_3$, -Cl, -Br, -$NO_2$

**Keywords** Azo; azo benzene; ester; mesophase; nematic; smectic

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## Introduction

Liquid-crystalline materials, either low molar mass or polymeric in nature, containing an azo group in the mesogenic core, are often studied from the point of view of their interesting optical properties, which enable application in, for example, optical switching, holography, and optical storage devices [1–6]. Azo dyes are also being used in liquid-crystal display devices for the guest–host interaction [7].

Aromatic azo-containing compounds (Ar−N=N−Ar′) can undergo a much easier photoinduced trans-cis isomerization than the C=C bond and thus can generate more interesting photoactive liquid crystals (LCs). Among these photoactive mesogenic units, azobenzene derivatives are most extensively investigated. The rigid rod-like structure of azobenzene molecules makes them suitable candidates for exhibiting liquid crystallinity [8,9]. On the other hand, the unique characteristics of azobenzene molecules provide the possibility of molecular motion in response to light or heat and thus offer many opportunities in photonic applications. In such azo-containing liquid-crystalline materials, the azo-containing moiety is usually incorporated into the side chain of the polymer backbone to induce the formation of LCs [10–15].

Azo compounds have the following advantages over substances with other linkages such as ester, tolane, or Schiff's base. Azo compounds are thermally very stable and are attractive from the point of view of studying photoinduced effects [16].

For potential commercial applications, the existence of mesophases at lower temperatures is of very high importance. Lateral substitution by a methyl group was used for some of these azo compounds in order to decrease the phase transition temperatures [17].

Most of the studies have been on Schiff bases or esters containing benzene or biphenyl units; comparatively few studies have been done on the influence of a naphthalene core on mesomorphism. Gray [18] has reported that 6-n-alkoxy-2-naphthanoic acids are mesomorphic, whereas 1,4- and 1,5-alkoxy naphthoic acids are non-mesomorphic. Dave and coworkers [19–21] have synthesized a number of 4-n-alkoxy-1-naphthylidene Schiff bases and cholesteryl naphthoates and studied their mesomorphism. Interest in naphthalene LC cores has revived in the last decade, as indicated by a significant number of research papers [22–30]. Recently, Prajapati *et al.* have reported few mesogenic homologous series of Schiff's base ester [31–33] and azo-esters [34–36] containing naphthalene moiety.

Demus and Sackmann [37] have reported mesomorphic azo ester dyes having a biphenyl core. Arora and Fergason [38] and Dave and Menon [39] have reported the azo ester dyes with different terminal substitutions. Vora and Dixit [40] have reported a homologous series containing an azo ester linking group and lateral substitution. In recent years Bubnov *et al.* [41] have reported azo-ester-based new ferroelectric liquid-crystalline compounds derived from chiral S-lactic acid as a terminal moiety. Prasad and Jákli [42] have synthesized azo-ester-based liquid crystals of achiral bent core and observed photoinduced effects in antiferroelectric tilted smectic mesophase. Long and Lin [43] also have synthesized and evaluated azo dye compounds and show variation of mesogenic behavior with the length of alkyl chains. Liquid crystal polymers that contain an azo-ester linkage in the main chain have also been synthesized [44].

Therefore, in the present work an attempt has been made to study the thermal stabilities of azomethine-azo and ester-azo central linkages. This led us to prepare more such compounds that would help further in understanding the effect of substitution of lateral and terminal groups on mesomorphism. In the present work we have selected two alkoxy chains such as octyl and hexadecyl, viz. 4-(4′-n-alkoxy benzylidene amino)-naphthalene-1-azo-benzene (series A) and 4-(4′-n-alkoxy benzoyloxy)-3-methyl-1-4″ substituted-1-azobenzene (series B) comprising azomethine-(-CH=N)-azo(-N=N) and ester (-COO)-azo(-N=N) linkages for synthesis. These two types of compounds also contain a lateral methyl (-$CH_3$) group at the 2′-position and 2′,3′-position fused ring system and they also consist of terminal chloro (-Cl), bromo (-Br), methyl(-$CH_3$), methoxy (-O $CH_3$), and nitro (-$NO_2$) groups. We have synthesized these compounds to study the influence of the lateral, as well as terminal group and also central linkages on mesomorphism and thermal stabilities of these compounds.

## Experimental

### Reagents and Technique

4-Hydroxy benzaldehyde, and α-naphthylamine were obtained from Merck, Germany. Benzoic acid, alkyl bromide (Lancaster, England). 4-Hydroxy o-Cresol, aniline, p-toludine, p-anisidine, p-chloroaniline, p-bromoaniline, and p-nitroaniline were provided by Nova Dyes Stuff [P] Ltd., Surat and used without further purification. The solvents were used after purification using the standard methods described in the literature [45].

Elemental analyses (C, H, N) were performed at Central Drugs Research Institute (CDRI) Lucknow. Infrared spectra were recorded with a Perkin-Elmer 2000 Fourier transform infrared (FTIR) spectrophotometer (S.A.I.F), Punjab University, Chandigarh in the frequency range 4000–400 $cm^{-1}$ with samples embedded in KBr discs. $^1H$ nuclear magnetic resonance (NMR) spectra of the compounds were recorded with a JEOL-GSX-400 using $CDCl_3$ as a solvent and TMS as an internal reference, and mass spectra (EI) of the compounds at Sofisticated Analytical Instrument Facilities (SAIF), IIT Madras, Chennai. Thin-layer chromatography analyses were performed by using aluminum-backed silica-gel plates (Merck 60 F524) and examined under short-wave ultraviolet (UV) light.

The phase-transition temperatures were measured using a Shimadzu DSC-50 at heating and cooling rates of 5°C $min^{-1}$. The optical microscopy studies were carried out with a Leitz Loborlux 12 POL (Wetzler, Germany)polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and coverslip.

### Synthesis

**Synthesis of 4-alkoxy benzaldehydes.** 4-Alkoxy benzaldehydes were prepared by a reported method [46–49]. The m.p. of these compounds was compared with reported values and they are very similar.

**Synthesis of 4-amino-naphthalene-4″-substituted-1-azobenzene.** These dyes were prepared by condensing α-naphthylamine with diazonium salts of substituted aniline. First the substituted anilines were diazotized with dilute HCl and $NaNO_2$

at 0–5°C and coupled with α-naphthylamine. Then the reaction mixture was neutralized with diluted NaOH, and the obtained precipitate was collected by filtration and then air dried. The crude compounds were purified by repeated recrystallizations using ethanol as solvent [50–51].

*Synthesis of 4-(4′-n-alkoxy benzylidene amino)-naphthalene-4″-substituted-1-azobenzene (series A).* A mixture of 1 mmol 4-alkoxy benzaldehyde and 4-amino-naphthalene-4″-substituted-1-azobenzene and three drops of acetic acid in absolute ethanol were heated at reflux for 4 h. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected and recrystallized from technical ethanol. The product was purified by column chromatography using a mixture of hexanes/ethyl acetate (7/1) as eluent. The above procedure was adopted for the synthesis of mesogenic dyes having terminal substitutions such as methyl, methoxy, chloro, and flouro azobenzene [52–54].

*$A_5$: Molecular formula: $C_{31}H_{32}ON_3Br$.* Elemental analysis, calculated for C 68.63% H 5.90%, and N 7.75%; found: C 68.95%, H 5.78%, and N 7.94%, EI-MS m/z (rel.int%): 541 $(M)^+$ FTIR (in KBr), 2864, 2925 $cm^{-1}$ (C-H aliphatic), 1602 $cm^{-1}$ (-C=N of azomethine), 1575–1515 $cm^{-1}$ (C=C aromatic ring stretching), 1470 $cm^{-1}$ (C–H bending of $CH_2$), 1166 $cm^{-1}$ (C–O–C); 1025 $cm^{-1}$ (C–O stretching); $^1$H-NMR ($CDCl_3$, δ, ppm): 0.87–0.92 (3H, t, $CH_3$, alkyl chain), 1.24–1.87 (m, -$(CH_2)$n, alkyl chain), 4.03–4.07 (2H, t, -$CH_2O$, alkoxy chain), 7.03–7.98 (m, phenyl protons), 8.49 (s, CH=N, aldehydic), 8.40–8.43 (d), and 8.95–8.98 (d) aromatic ortho proton of first ring).

*$A_8$: Molecular formula: $C_{40}H_{51}O_2N_3$.* Elemental analysis, calculated for C 79.33%, H 8.40%, and N 6.94%; found: C 79.32%, H 8.40%, and N 6.91%. EI-MS m/z (rel.int%): 606 $(M+1)^+$ FT-IR (in KBr), 2858, 2911 $cm^{-1}$ (C–H aliphatic), 1602 $cm^{-1}$(-C=N of azomethine), 1575–1514 $cm^{-1}$ (C=C aromatic ring stretching), 1480 $cm^{-1}$ (C–H bending of $CH_2$), 1166 $cm^{-1}$ (C-O-C), 1030 $cm^{-1}$ (C–O stretching); $^1$H-NMR ($CDCl_3$, δ, ppm): 0.87–0.92 (3H, t, $CH_3$, alkyl chain), 1.24–1.87 (m, -$(CH_2)$n, alkyl chain), 3.91 (s, terminal –$OCH_3$ proton attached to the aromatic ring), 4.03–4.07 (2H, t, -$CH_2O$, alkoxy chain), 7.03–7.98 (m, phenyl protons), 8.49 (s, CH=N azomethine), 8.40–8.43 (d), and 8.95–8.98 (d) (aromatic ortho proton of first ring).

***Synthesis of 4-n-Alkoxy Benzoic Acids.*** 4-n-Alkoxy benzoic acids were prepared as reported by Dave and Vora [55]. The m.p. of these compounds was compared with the reported values and they are very similar.

***Synthesis of 4-n-Alkoxy Benzoyl Chlorides.*** 4-n-alkoxy benzoyl chlorides were prepared by the reported method [55]. The m.p. of these compounds was compared with the reported values and they are very similar.

***Synthesis of 4-hydroxy-3-methyl-1-azobenzene.*** A well-stirred mixture of aniline (0.01 mol, 0.93 g) and concentrated HCl (0.03 mol, 3.6 mL) was cooled below 0–5°C and a solution of $NaNO_2$ (0.01 mol, 0.7 g) in water (5 mL) was added dropwise in such a way that the temperature of the mixture was in the range 0–5°C. The cold, dark solution was added dropwise to a cold mixture of o-cresol (0.01 mol, 1.08 g), NaOH (20% w/v) during which the temperature of the mixture was maintained below 0–5°C. Acidification with aqueous HCl furnished the crude product, which was collected by filtration, dried in air, and crystallized several times from ethanol [56].

***Synthesis of 4-(4′-n-alkoxy benzoyloxy)-3-methyl-1-azobenzene*** *(series B).* 4-Hydroxy-3-methyl-1-azobenzene (0.01 mol, 1.98 g) was dissolved in dry pyridine (10 mL) and was added dropwise with occasional stirring into ice-cold 4-n-alkoxy benzoyl chloride (0.01 mol, 2.69 g) in a round-bottom flask. Then the mixture was refluxed in a hot water bath for 2 h and allowed to stand overnight. The mixture was acidified with cold 1:1 diluted hydrochloric acid to precipitate the product. The solid obtained was filtered, washed with water, saturated sodium bicarbonate solution, and again water and thus the crude azo dye obtained. The solid ester azo dye was recrystallized from acetic acid until constant transition temperature was obtained [55]. The above procedure was adopted for the synthesis of mesogenic dyes having terminal substituents such as methyl, methoxy, chloro, flouro, and nitro azobenzene.

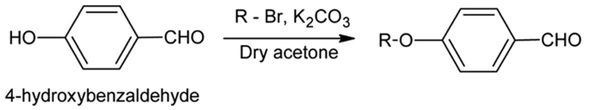
*$B_1$: Molecular formula: $C_{28}H_{32}O_3N_2$.* Elemental analysis: calculated for C 75.68%, H 7.10%, and N 6.31%; found: C 75.96%, H 7.45%, and N 6.58%. EI-MS m/z (rel.int%): 443 $(M\text{-}1)^+$ FTIR (in KBr), 2864, 2925 $cm^{-1}$ (C−H aliphatic), 1737 $cm^{-1}$(-C=O of ester), 1575–1515 $cm^{-1}$ (C=C aromatic ring stretching), 1470 $cm^{-1}$ (C−H bending of $CH_2$); 1273 $cm^{-1}$ (C−O stretching of ester), 1172 $cm^{-1}$ (C−O−C); $^1H$-NMR ($CDCl_3$, $\delta$, ppm): 0.87–0.91 (3H, t, $CH_3$, alkyl chain), 1.26–1.87 (m, -$(CH_2)n$, alkyl chain), 2.33 (s, lateral −$CH_3$ proton attached to the aromatic ring), 4.03–4.07 (2H, t, -$CH_2O$, alkoxy chain), 6.97–8.20 (m, phenyl protons).

*$B_7$: Molecular formula: $C_{36}H_{48}O_3N_2$.* Elemental analysis: calculated for C 77.70%, H 8.63%, and N 5.04%; found: C 77.95%, H 8.85%, and N 5.33%. EI-MS m/z (rel.int%): 556 $(M)^+$ FTIR (in KBr), 2864, 2932 $cm^{-1}$ (C−H aliphatic), 1730 $cm^{-1}$(-C=O of ester), 1575–1515 $cm^{-1}$ (C=C aromatic ring stretching), 1480 $cm^{-1}$ (C−H bending of $CH_2$); 1273 $cm^{-1}$ (C−O stretching of ester), 1179 $cm^{-1}$ (C−O−C); $^1H$-NMR ($CDCl_3$, $\delta$, ppm): 0.87–0.91 (3H, t, $CH_3$, alkyl chain), 1.26–1.87 (m, -$(CH_2)n$, alkyl chain), 2.33 (s, lateral −$CH_3$ proton attached to the aromatic ring), 4.03–4.07 (2H, t, −$CH_2O$, alkoxy chain), 6.97–8.20 (m, phenyl protons).

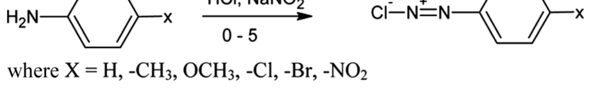
## Synthesis

### SCHEME 1

***Preparation of 4-alkoxy benzaldehydes***

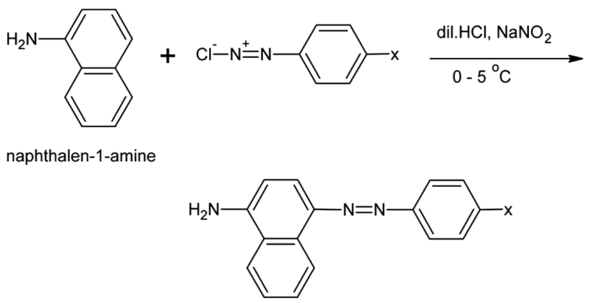


***Diazotization of aniline***



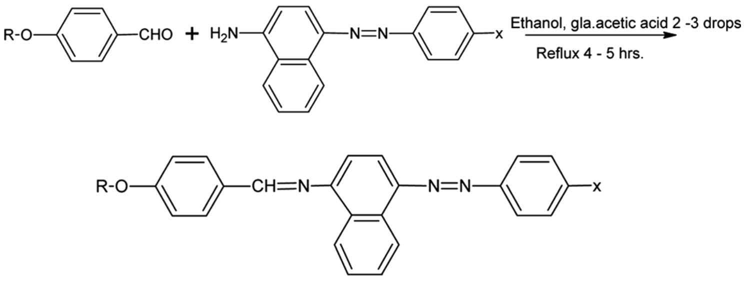
where X = H, -$CH_3$, $OCH_3$, -Cl, -Br, -$NO_2$

### *Synthesis of 4-amino-naphthalene-1-azobenzene*



where X = H, $-CH_3$, $OCH_3$, -Cl, -Br, $-NO_2$

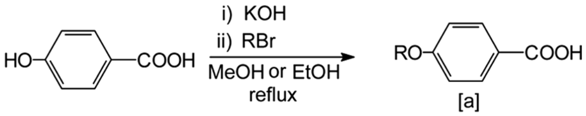
### *Synthesis of 4-(4′-n-alkoxy benzylidene amino)-naphthalene-1-azo-benzene (Series A)*



where R = $C_8H_{17}$, $C_{16}H_{33}$, X = H, $-CH_3$, $OCH_3$, -Cl, -Br, $-NO_2$

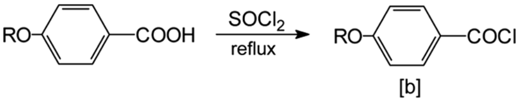
## SCHEME 2

### *Synthesis of 4-n-alkoxy benzoic acids*



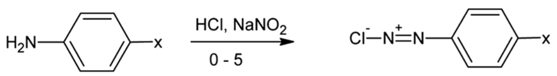
where R = $C_8H_{17}$ and $C_{16}H_{33}$

### *Synthesis of 4-n-alkoxy benzoyl chlorides*



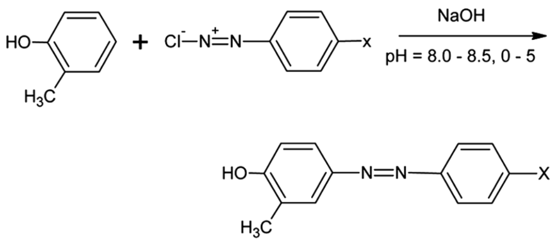
where R = $C_8H_{17}$ and $C_{16}H_{33}$

### *Diazotization of Aniline*



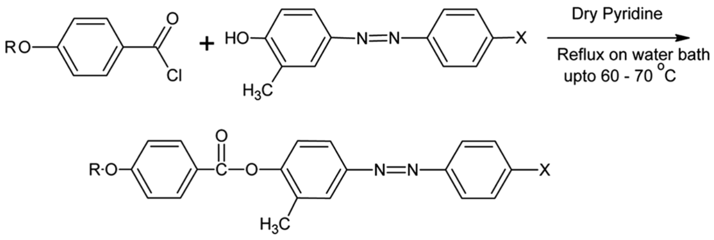
where X = H, -$CH_3$, $OCH_3$, -Cl, -Br, -$NO_2$

### *Synthesis of 4-hydroxy-3-methyl-1-azobenzene*



where X = H, -$CH_3$, $OCH_3$, -Cl, -Br, -$NO_2$

### *Synthesis of 4-(4′-n-alkoxy benzoyloxy)-3-methyl-1-azobenzene (Series B)*



where R = $C_8H_{17}$, $C_{16}H_{33}$, X = H, -$CH_3$, $OCH_3$, -Cl, -Br, -$NO_2$

## Results and Discussion

In order to investigate the influence of the terminal substitution on mesomorphism two new series, viz. 4-(4′-n-alkoxy benzylidene amino)-naphthalene-4″-substituted-1-azo-benzene (series A) containing azo-schiff base as a central linkage and 4-(4′-n-alkoxy benzoyloxy)-3-methyl-1-4″ substituted-1-azobenzene (series B) containing azo-ester as a central linkage and different terminal substitutions, were synthesized and their mesomorphic properties were studied. The common structural features of the compounds are that they consist of the same terminal substitutent at one end. The mesomorphic properties of all the synthesized compounds have been characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) attached with a Mettler hot stage.

The transition temperatures of both series are given in Tables 1 and 2. In series A compounds $A_1$ and $A_3$ exhibit only a nematic mesophase, whereas compounds $A_2$,

**Table 1.** Transition temperatures of Series A

| | | | Transition temperature (°C) | | |
|---|---|---|---|---|---|
| Compounds | R = n-Alkoxy | X | S | N | I |
| $A_1$ | Octyloxy | -H | — | 103[a] | 108 |
| $A_2$ | Octyloxy | $-CH_3$ | 111 | 126 | 175 |
| $A_3$ | Octyloxy | $-OCH_3$ | — | 107 | 205 |
| $A_4$ | Octyloxy | -Cl | 115 | 122 | 179 |
| $A_5$ | Octyloxy | -Br | 108 | 130 | 174 |
| $A_6$ | Hexadecyloxy | -H | 65 | 74 | 94 |
| $A_7$ | Hexadecyloxy | $-CH_3$ | 68 | 82 | 140 |
| $A_8$ | Hexadecyloxy | $-OCH_3$ | 92 | 112 | 163 |
| $A_9$ | Hexadecyloxy | -Cl | 82 | 128 | 149 |
| $A_{10}$ | Hexadecyloxy | -Br | 80 | 131 | 150 |

[a] Monotropic mesophase.

$A_4$, $A_5$, $A_6$, $A_7$, $A_8$, $A_9$, and $A_{10}$ exhibit a smectic as well as a nematic phase. In series A compounds $A_1$ is monotropic, whereas the rest of the compounds are enantiotropic in nature. In series B compounds $B_1$ to $B_9$ exhibit only a nematic mesophase, and compounds $B_{10}$ and $B_{11}$ exhibit a smectic as well as a nematic phase, but compound $B_{12}$ exhibits only a smectic phase.

DSC is a valuable method for the detection of phase transitions. It yields quantitative results; therefore, we may draw conclusions concerning the nature of the phases that occur during the transition. In the present study, enthalpies of two derivatives of series A and series B were measured by DSC. DSC data for series A and series B are recorded in Tables 3 and 4, which helps to further confirm the mesophase type. Table 3 shows the phase transition temperatures, associated enthalpy ($\Delta H$), and molar entropy ($\Delta S$) for compounds of series A ($A_2$, $A_4$, $A_5$, and $A_7$) and

**Table 2.** Transition temperatures of Series B

| | | | Transition temperature (°C) | | |
|---|---|---|---|---|---|
| Compounds | R = n-Alkoxy | X | S | N | I |
| $B_1$ | Octyloxy | -H | — | 67 | 91 |
| $B_2$ | Octyloxy | $-CH_3$ | — | 85 | 161 |
| $B_3$ | Octyloxy | $-OCH_3$ | — | 96 | 198 |
| $B_4$ | Octyloxy | -Cl | — | 77 | 170 |
| $B_5$ | Octyloxy | -Br | — | 81 | 160 |
| $B_6$ | Octyloxy | $-NO_2$ | — | 111 | 201 |
| $B_7$ | Hexadecyloxy | -H | — | 63 | 83 |
| $B_8$ | Hexadecyloxy | $-CH_3$ | — | 76 | 134 |
| $B_9$ | Hexadecyloxy | $-OCH_3$ | — | 81 | 154 |
| $B_{10}$ | Hexadecyloxy | -Cl | 78 | 117 | 140 |
| $B_{11}$ | Hexadecyloxy | -Br | 91 | 106 | 136 |
| $B_{12}$ | Hexadecyloxy | $-NO_2$ | 86 | — | 161 |

**Table 3.** DSC data for Series A compounds

| Series | Compound | Transition | Peak temp. (microscopic temp.) (°C) | ΔH ($Jg^{-1}$) | ΔS ($Jg^{-1}K^{-1}$) |
|---|---|---|---|---|---|
| A | $A_2$ | Cr-S | 112 (111) | 97.80 | 0.2547 |
| | | S-N | 124.29 (126) | 14.57 | 0.0367 |
| | | N-I | 175 (175) | 2.10 | 0.0047 |
| | $A_4$ | Cr-S | 115 (115) | — | — |
| | | S-N | 125.54 (122) | 70.66 | 0.1773 |
| | | N-I | 179 (179) | 1.94 | 0.0043 |
| | $A_5$ | Cr-S | 108 (108) | 7.69 | 0.0202 |
| | | S-N | 131 (130) | 64.36 | 0.1593 |
| | | N-I | 174 (174) | 1.35 | 0.0030 |
| | $A_7$ | Cr-S | 72 (68) | 6.28 | 0.0182 |
| | | S-N | 81.37 (82) | 32.81 | 0.0926 |
| | | N-I | 137.59 (140) | 1.55 | 0.0038 |
| | $A_9$ | Cr-S | 81.96 (82) | 47.55 | 0.1339 |
| | | S-N | 128 (128) | — | — |
| | | N-I | 145 (149) | 1.45 | 0.0034 |
| | $A_{10}$ | Cr-S | 85 (80) | 92.98 | 0.2597 |
| | | S-N | 132 (131) | — | — |
| | | N-I | 144.57 (150) | 1.40 | 0.0034 |

Table 4 shows the phase transition temperatures, associated enthalpy (Δ*H*), and molar entropy (Δ*S*) for compounds of series B ($B_2$, $B_4$, $B_5$, $B_8$, and $B_{10}$). Enthalpy values of the various transitions agree well with the existing related literature values [57]. The DSC curves of representative compounds are shown in Figs. 1 to 4. Microscopic transition temperature values are very similar to the DSC data.

A number of homologues were synthesized constituting a p-phenylene unit to study the effect of chemical constitution on liquid-crystalline properties. There is a very delicate balance between the chemical constitution and liquid-crystalline

**Table 4.** DSC data for Series B compounds

| Series | Compound | Transition | Peak temp. (microscopic temp.) (°C) | ΔH ($Jg^{-1}$) | ΔS ($Jg^{-1}K^{-1}$) |
|---|---|---|---|---|---|
| B | $B_2$ | Cr-N | 83.51 (85) | 49.76 | 0.1396 |
| | | N-I | 162.6 (161) | 3.17 | 0.0073 |
| | $B_4$ | Cr-N | 82 (77) | 78.47 | 0.2210 |
| | | N-I | 165 (170) | 1.94 | 0.0044 |
| | $B_5$ | Cr-N | 78.5 (81) | 78.64 | 0.2237 |
| | | N-I | 158 (160) | 3.17 | 0.0074 |
| | $B_8$ | Cr-N | 78.2 (76) | 35.11 | 0.1000 |
| | | N-I | 130.7 (134) | 2.11 | 0.0052 |
| | $B_{10}$ | Cr-S | 81 (78) | 33.63 | 0.1000 |
| | | S-N | 118 (117) | — | — |
| | | N-I | 136.66 (140) | 1.67 | 0.0041 |

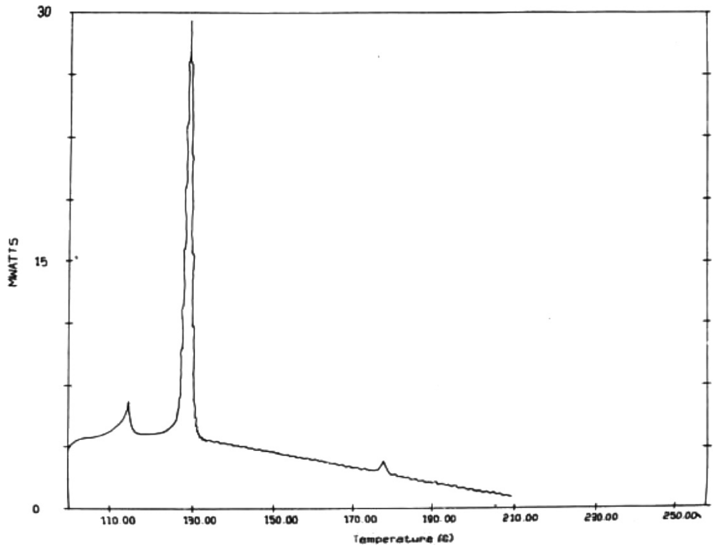


**Figure 1.** DSC curve of compound $A_4$.

properties. Generally the introduction of a lateral substituent is different for all types of mesophases. In the quest of obtaining low melting liquid crystals with broad mesophase range, it was noted that a lateral substituent like chloro (-Cl) or methyl ($-CH_3$) is quite effective in reducing crystal mesophase temperature to give low melting liquid crystals [58–60].

In light of this, it was of interest to introduce lateral methyl and terminal halogens (-Cl, -Br), methyl, methoxy, and nitro substituents on the benzene ring at

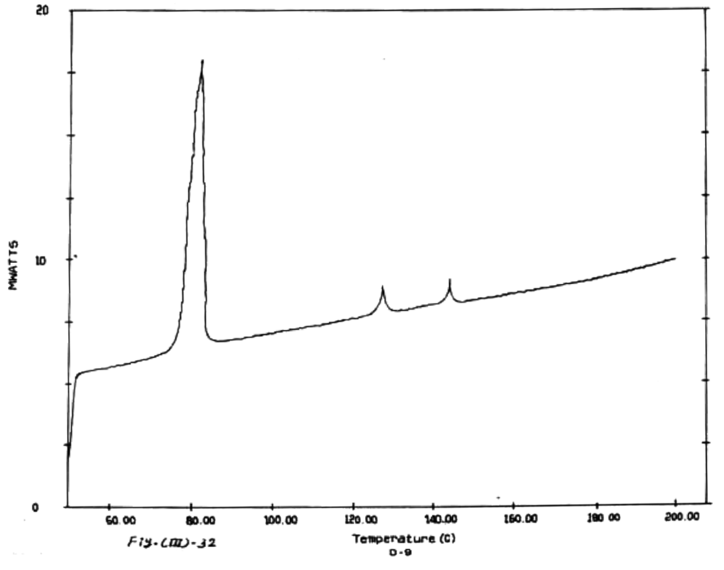


**Figure 2.** DSC curve of compound $A_9$.

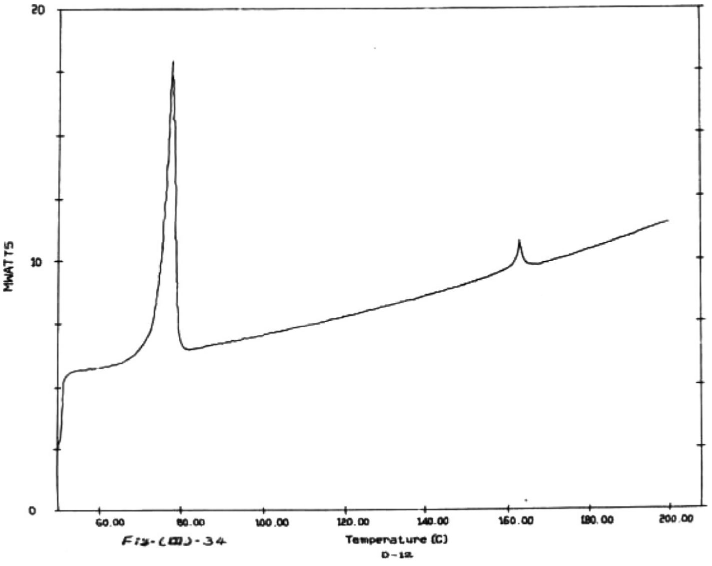


Figure 3. DSC curve of compound $B_2$.

one end of the p-phenylene system to evaluate the effect of substituents on mesomrphic behavior.

In series A 10 compounds were synthesized, out of which $A_1$-$A_5$ have an octyloxy ($OC_8H_{17}$) chain and $A_6$-$A_{10}$ have a hexadecyloxy ($-OC_{16}H_{33}$) chain, in addition to different terminal subsituents like –H, $-CH_3$, $-OCH_3$, -Cl, and -Br. In series B 12 compounds were synthesized, of which $B_1$-$B_6$ have an octyloxy ($OC_8H_{17}$) chain and $B_7$-$B_{12}$ have a hexadecyloxy ($-OC_{16}H_{33}$) chain; in addition to different terminal subsituents like –H, $-CH_3$, $-OCH_3$, -Cl, -Br, and $-NO_2$.

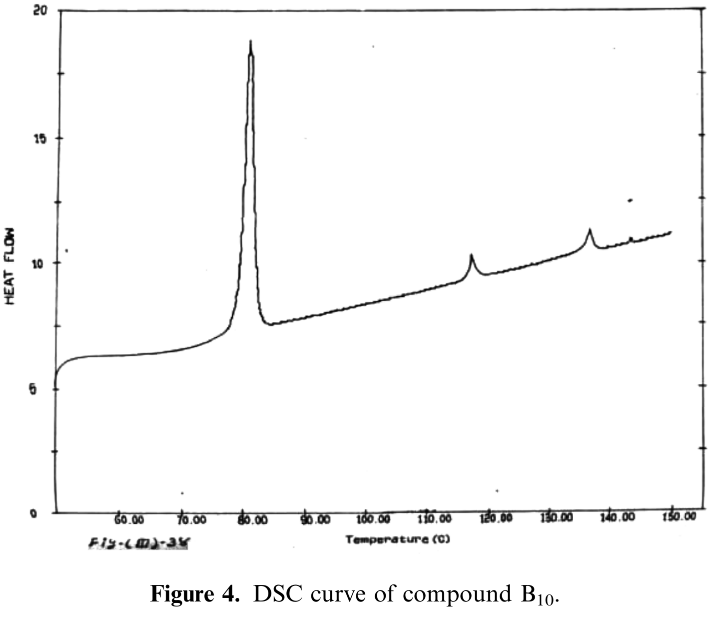


Figure 4. DSC curve of compound $B_{10}$.

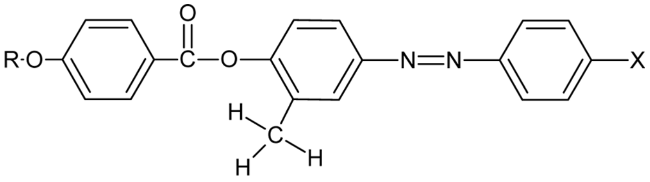
## Thermal Stability

The average thermal stability of the compounds of series A, that is, azomethine-based azo dyes, is higher than compounds of series B, that is, ester-based azo dyes. Because both series have the same terminal subsituents at one end and of the other end a n-alkoxy chain. The two types of compounds differ only in the central linkage and lateral substitution. Compounds of series A have an azomethine (-CH=N)-azo(-N=N) central linkage and a lateral substituted benzene ring that is closed at the 2′,3′-position of the central unit, whereas compounds of series B have an ester (-COO)-azo(-N=N) central linkage and a lateral substituted methyl group at the 3′-position of the central unit.

The presence of a naphthalene unit as the central unit in series A shows that the naphthalene compounds give rise to higher melting points, more stable mesophases, and wider liquid-crystalline phase ranges in comparison with their phenyl analogues. These properties are a direct consequence of the molecular arrangement in both the solid and the liquid-crystal phases. As mentioned earlier, the phenyl and naphthyl central core units differ mainly in their length and extension of the electronic conjugation. The increased transition temperatures can clearly be attributed to the increased length and higher polarizability of the naphthalene structure that allows both stronger and wider-ranging molecular interaction.

The introduction of the lateral methyl group in series B compounds changes the molecular conformation and broadens the molecules, which decreases, the transition temperature of all phases. This factor is a direct result of an increase in the breath or thickness of the molecule [61]. Thus, the introduction of the lateral methyl group results in decreased transition temperature of all phases in the series B compounds. This has been attributed to the broadening of the molecules as well as the change in molecular conformation. The increased dissymmetry resulting from the lateral methyl group leads to less effective packing in the crystal lattice and therefore lowers the crystal to mesophase transition temperature as shown in Tables 1 and 2.

As mentioned earlier, series A has the central azomethine (-CH=N-) group, whereas series B has the central carboxy (-COO-) group. The oxygen atom of this central carboxy group in the molecules of series B will bump into the nonbonded side of the adjacent –H of the aromatic ring, thereby causing considerable strain on the molecule. This will cause some twist around the C-O bond and force the benzene ring out of the plane of the molecule and broaden the molecule [58] as shown below.



The H atom of the central azomethine (-CH=N-) group will also behave in the same way and bring about the twist in the molecules of series A, but the twist in this case will be much less than in the molecules of series B. Hence, the molecules of series B will be more non-coplanar than those of series A. This effect is observed in the present case where the thermal stabilities of series B compounds are less than those of series A compounds.

The N-I average thermal stability order with respect to the terminal group in series A compounds is observed as

$$\underset{(184^\circ C)}{OCH_3} > \underset{(164^\circ C)}{-Cl} > \underset{(162^\circ C)}{-Br} > \underset{(158^\circ C)}{-CH_3} > \underset{(101^\circ C)}{-H}$$

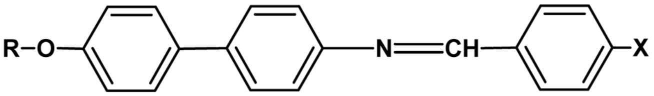
In the above order, it shows that N-I average thermal stability of the $-OCH_3$ group is higher than that of other terminal groups. This could be explained that in $-O\text{-}CH_3$ group, the lone pair of electrons of oxygen is shielded by an insulator-like methyl group. The repulsive forces involving the oxygen lone pairs are thereby substantially reduced and allow a close approach of the neighboring molecules, increasing bonding forces. This leads to an increase in the N-I transition temperature. The N-I thermal stability of $-CH_3$ is less than that of $-Cl$ and $-Br$ groups. This is because the $-CH_3$ group is less polar, whereas the $-Cl$ and $-Br$ groups will endow the molecule with higher polarity, high terminal attraction, and hence higher N-I average thermal stability. The same trend was observed by Gray *et al.* [18,62] and Coates [63].

In series A mesogenic compounds, the S-N average thermal stability of terminal group is observed only in both the chain as it shows that is series-A compounds $A_1$-$A_5$ having octyloxy chain and compounds $A_6$-$A_{10}$ having hexadecyloxy chain. In both octyloxy and hexadecyloxy chain the terminal substituents are $-Br$, $-Cl$, & $CH_3$ in which average smectic-nematic thermal stabilities is given in order.

$$\underset{(130.5^\circ C)}{-Br} > \underset{(125^\circ C)}{-Cl} > \underset{(104^\circ C)}{-CH_3}$$

The above order shows that terminal $-CH_3$ substituted compounds are less mesomorphic than those with $-Cl$ and $-Br$ units. This is because $-CH_3$ less polar, whereas the $-Cl$ and $-Br$ groups endow the molecules with high polarity, greater terminal attraction, and hence higher S-N thermal stability. Enhanced smectic tendencies have been found by Gray *et al.* [18] for the 4′-bromo and 4′-chloro derivatives relative to the unsubstituted compound.

Gray [18] has given the order of decreasing smectic thermal stability of the compounds in terms of the terminal substituents $-X-$ as



$NHCOCH_3 > Br > Cl > F > NO_2 > NMe_2 > n\text{-}PnO > n\text{-}PrO > Me > H > OMe$

This order indicates no simple relationship between the strength of the dipole and smectic thermal stability. Thus, the nitro group with its strong dipole acting along the long axis of the molecule yields a smectic mesophase that is less thermally stable than that of X=Cl. Also, with no terminal dipole X=H, the smectic mesophase is thermally more stable than for X=-OCH$_3$, for which the dipole acts at an angle across the long axis of the molecule. This fact suggests that terminal dipoles contribute to the terminal intermolecular attractions, either by polarization or dipole–dipole interactions as well as the lateral attractions. If such terminal attraction occurs, the contribution of the dipole to the lateral attraction will be decreased and the balance of the lateral and

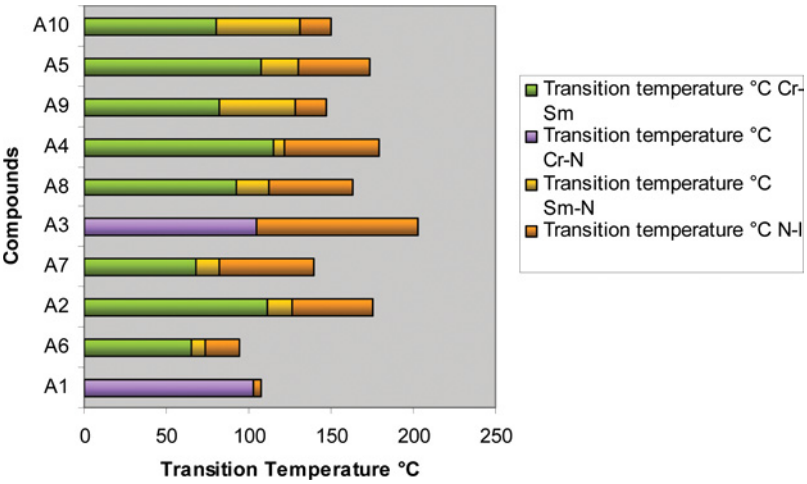


**Figure 5.** Plot of the mesomorphic behavior of compounds $A_1$ to $A_{10}$.

terminal cohesion will be affected. The determination of the smectic characteristics of the molecules is therefore complicated by the possible dual role of these dipoles in affecting both terminal and lateral attractions. The relative span of temperature of various p-substituted groups of series A and series B compounds is shown in Figs. 5 and 6. The mesophase textures observed are shown in Fig. 7.

### Commencement of Smectic Mesophase

In series B compounds, the smectic phase commences late at the hexadecyl derivatives of alkyl chain, whereas it commences at the octyl and hexadecyl derivative

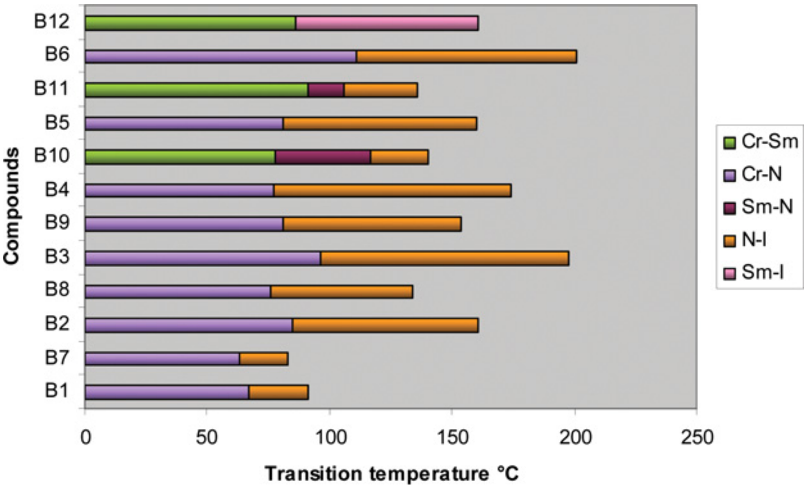


**Figure 6.** Plot of the mesomorphic behavior of compounds $B_1$ to $B_{12}$.

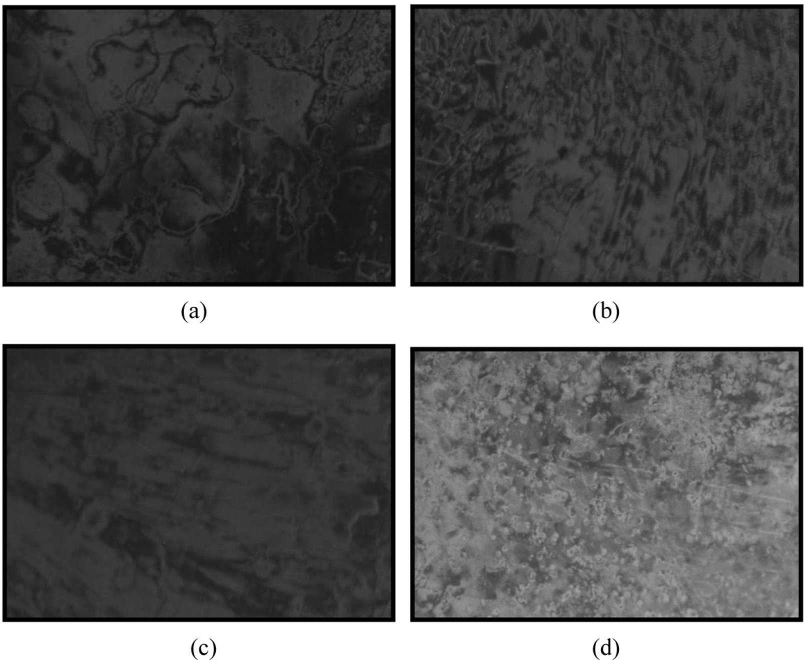


**Figure 7.** (a) Texture of nematic phase of $A_4$ of series A at 122°C on cooling. (b) Thread-like texture of the nematic phase of $A_{10}$ of series A at 131°C on cooling. (c) Marble texture of the nematic phase of $B_1$ of series B at 67°C on cooling. (d) Marble texture of the nematic phase of $B_9$ of series B at 81°C.

respectively in series A. It is rather difficult to postulate the exact commencement of the smectic mesophase in the compounds of series A because it depends on a number of factors like polarizability, breath (thickness), and geometry of the molecules.

The difference between the two types of compounds is in the central groups. In series A compounds have an azomethine (-CH=N-) group and naphthalene nucleus, which make the molecules longer and more polarized. Thus, early commencement of a smectic phase in series A can be understood. Series B has a central ester (-COO) group and lateral substituted $-CH_3$ group. In series B the lateral $-CH_3$ group, which is ortho to –COO- linkage, will have twofold effects: (i) increasing the breath (thickness) of the molecules and (ii) reducing the coplanarity of the molecules. Both these effects explain the late commencement of the smectic mesophase and lower thermal stability of the compounds of series B.

From the above results it can be seen that not only the geometry of the molecules but also length, breath (thickness), and polarizability of the molecules play an important role in the mesomorphic behavior of compounds.

## Conclusion

In this article we have presented the synthesis and characterization of two new mesogenic series, viz. 4-(4′-n-alkoxy benzylidene amino)-naphthalene-4″-substituted-1-azo-benzene (series A) containing azo-Schiff base as a central linkage and 4-(4′-n-alkoxy benzoyloxy)-3-methyl-1-4″ substituted-1-azobenzene (series B) containing azo-ester as a central linkage and different terminal substitutions. The presence of a naphthalene nucleus as a central unit in series A shows that the naphthalene compounds give rise to higher melting points, higher mesophase stability, and wider liquid-crystalline phase ranges in comparison with their phenyl analogues. These properties are a direct consequence of the molecular arrangement in both the solid and the liquid-crystal phases. The phenyl and naphthyl central core units differ mainly in their length and extension of the electronic conjugation. The increased transition temperature can clearly be attributed to the increased length and higher polarizability of the naphthalene structure that allows both stronger and wider-ranging molecular interactions. The introduction of the lateral methyl group in series B compounds changes the molecular confirmation and broadening of the molecules, which decreases the transition temperatures of all phases. The increased dissymmetry resulting from the lateral methyl group leads to less effective packing in the crystal lattice and therefore lowers the crystal mesomorphic transition temperature.

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