

Naphthalene azomesogens with terminal chloro groups

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A homologous series of azomesogens, with terminal chloro groups have been synthesized. All the homologous synthesized compounds exhibit enantiotropic nematic mesophase. The mesomorphic properties of the present series are compared with other structurally related series to evaluate the effect of terminal chloro group and its position on mesomorphism.

Keywords : Azomesogen, mesophase, nematic phase, Schiff base, azomethine

A vast number of mesogenic naphthalene derivatives are reported in the literature^{1,2}, as naphthalene derivatives exhibit rich mesomorphism if properly designed. Schiff base compounds are synthesized in large numbers as these compounds exhibit nematic and smectic mesophase^{3,4}. Wigned^{5,6} reported a few mesogenic Schiff bases of 2,6-, 1,5- and 1,4-diamino-naphthalenes.

Dave *et al.*⁷ reported the mesomorphic behaviour of homologous series obtained by condensing 4-*n*-alkoxy-1-naphthaldehydes with benzilene, *p*-phenylenediamine⁸, and *p*-amino benzoic acid⁹. Arora and Ferguson¹⁰ studied a benzylidene Schiff base series containing an azo group. In the last decade, a significant number of research papers on naphthalene LC cores appeared in the literature¹¹⁻²⁰. Recently, the synthesis and mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene have also appeared in the literature^{21,22}. Prajapati *et al.*²³ also reported mesogenic homologous series of Schiff base cinnamates comprising a naphthalene moiety and investigated the effect of an ethylene linking group (cinnamoyl linkage) and naphthalene moiety on the mesomorphic properties of such molecules. Thaker and Tandel²⁴ reported naphthalene core-based mesogens with terminal halogen substituents. As an extension of the work on naphthalene moiety, a new mesogenic homologous series of azo-Schiff base containing terminal multi-chloro groups have been synthesized to investigate their influence on mesomorphism.

Results and Discussion

Elemental analysis of the compounds synthesized is given in **Table I**, the values of C, H, N found are in close agreement with the calculated one.

Mesophase exhibited by series-1 compounds was identified by examining thin film of a sample sandwiched between a glass slide and a cover slip under an optical polarizing microscope. On cooling the isotropic liquid small droplets appeared which coalesce to classical schlieren (threaded) texture characteristic of the nematic phase.

Calorimetry is a valuable method for the detection of phase transition. It yields quantitative results; therefore it may be possible to draw conclusions concerning the nature of the phases, which occur during the transitions. In the present study, enthalpies of two derivatives of each series-1 were measured by differential scanning calorimetry. Data are recorded in **Table II**. Enthalpy values of the various transitions agree well with the literature value²⁵.

Series-1

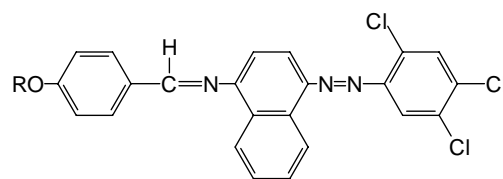
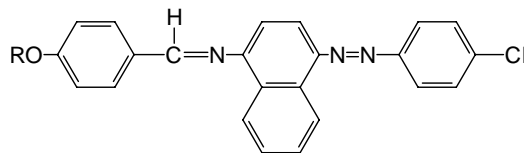
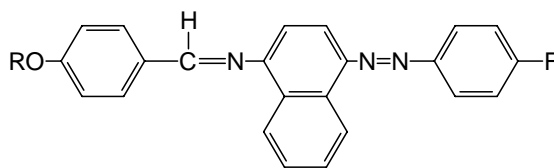
As can be seen in **Table III** the C₃ to C₈ tail display enantiotropic nematic phase and the higher homologues with C₁₀, C₁₂, C₁₄ and C₁₆ tail exhibit both smectic-A (**Figure 1a**) and nematic (**Figure 1b**) enantiotropic phases.

From the plot of transition temperatures against the number of carbon atoms (**Figure 2**), it can be noticed that Cr-M transition temperatures decreased with increase in the length of terminal alkoxy chain.

However, the odd-even effect of this series is not so pronounced. This is in agreement with the observation reported for such homologous series³.

Table IV shows the comparison of N-I transition temperatures range of N phase and molecular structure of representative compound **10** ($n=10$) of the present series-I and structurally related compounds **A** and **B** reported in the literature. It indicates that the width of N mesophase for compound **A** is 56°C and compound **10** is 59°C whereas N-I transition temperature for compound **A** is 168°C and that of compound **10** is 183.0°C. Gray³ has explained that a compound which requires more thermal energy to disorganize than the parallel molecular arrangement of the N melt is thermally more stable. The N mesophase range and the N-I transition temperature of compound **10** is higher by 3 and 12°C, respectively when compared with that of compound **A** and the Sm-N mesophase range of compound **10** are higher by

11°C, when compared with compound **A**. The compound **B** has fluoro substitution at the terminal benzene nucleus. On comparing the molecules of compound **B** with the molecules of compound **10**, the breadth has decreased due to the terminal fluoro group on benzene ring. It seems that the terminal

**10****A****B****Table I** — Elemental analysis for series-I compounds

Compd	R= C _n H _{2n+1} n	Mol. formulae <i>m/z</i>	Calcd % (Found)		
			C	H	N
1	3	C ₂₆ H ₂₀ N ₃ OCl ₃ 496.5	62.83 (62.89)	4.02 4.10	8.45 8.41
2	4	C ₂₇ H ₂₂ N ₃ OCl ₃ 510.5	63.46 (63.50)	4.30 4.25	8.22 8.19
3	5	C ₂₈ H ₂₄ N ₃ OCl ₃ 524.5	64.06 (64.10)	4.57 4.54	8.00 7.95
4	6	C ₂₉ H ₂₆ N ₃ OCl ₃ 538.5	64.62 (64.57)	4.82 4.87	7.79 7.74
5	7	C ₃₀ H ₂₈ N ₃ OCl ₃ 552.5	65.15 (65.11)	5.06 5.01	7.60 7.55
6	8	C ₃₁ H ₃₀ N ₃ OCl ₃ 566.5	65.66 (65.61)	5.29 5.24	7.41 7.46
7	10	C ₃₃ H ₃₄ N ₃ OCl ₃ 594.5	66.61 (66.58)	5.71 5.76	7.06 7.01
8	12	C ₃₅ H ₃₈ N ₃ OCl ₃ 622.5	67.46 (67.41)	6.10 6.15	6.74 6.76
9	14	C ₃₇ H ₄₂ N ₃ OCl ₃ 650.5	68.25 (68.21)	6.45 6.40	6.45 6.40
10	16	C ₃₉ H ₄₆ N ₃ OCl ₃ 678.5	68.97 (68.93)	6.77 6.72	6.19 6.13

Table III — Transition temperature (°C) of compounds of series-I
Sm= Smectic phase, N = Nematic phase, I = Isotropic

Compd	R= <i>n</i> -alkoxy	Transition temperature (°C)		
		Sm	N	I
1a	Propyl	•	-	-
1b	Butyl	•	147	230
1c	Pentyl	•	138	214
1d	Hexyl	•	143	206
1e	Heptyl	•	131	201
1f	Octyl	•	133	197
1g	Decyl	124	94	188
1h	Dodecyl	119	110	171
1i	Tetradecyl	128	103	166
1j	Hexadecyl	137	94	166

Table II — DSC data for series-I compounds

Compd	Transition	Peak temp °C	ΔH (Jg ⁻¹)	ΔS (Jg ⁻¹ K ⁻¹)	Total entropy change ΔS (Jg ⁻¹ K ⁻¹)
		Microscopic temp			
A₈	Cr→N	130.14(133)	107.5	0.266	0.135
	N→I	191.40(194)	2.722	0.005	
A₁₂	Cr→N	117.07(119)	127.0	0.310	0.162
	N→I	167.07(171)	6.383	0.014	

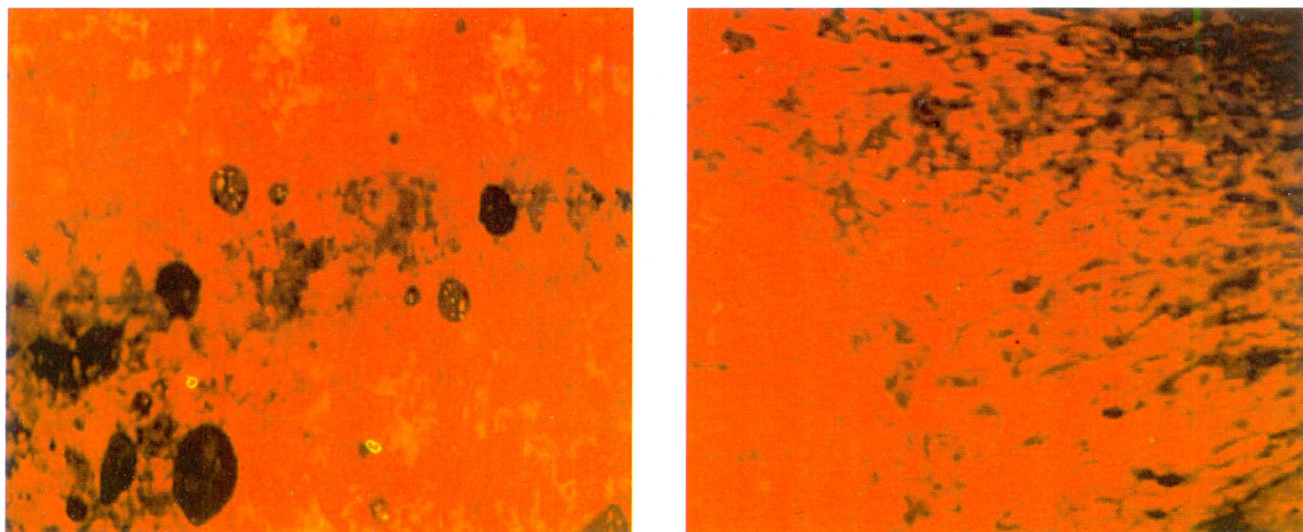


Figure 1 — Texture of compound C_{10} (1g) (a) Smectic -A at 124°C and (b) Nematic phase at 94°C

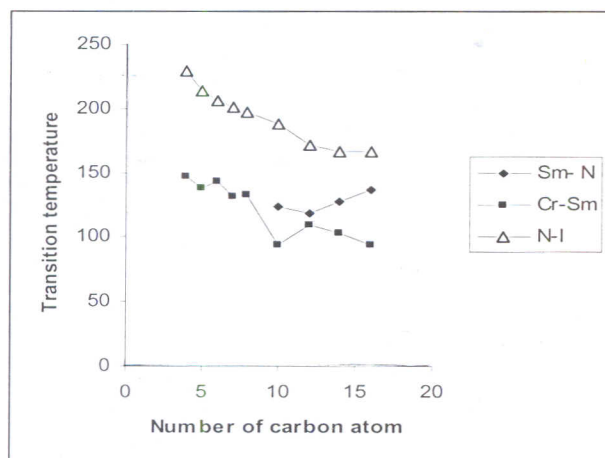


Figure 2 — Transition temperature vs number of carbon atom

Table IV — Different transition temperatures and range of mesophases observed in series A and B

Compd	Cr	Sm	N	I	Sm-N mesophase range (°C)	N-I mesophase range (°C)
10	•	94	124	183	30	59
A	•	83	112	168	29	56
B	•	-	112	147	-	35

Cr= Crystalline, Sm= Smectic phase, N = Nematic phase, I = Isotropic

fluoro group not only decreases the breadth of the molecule of compound **10** but also decreases the acoplanarity in the system due to steric interaction. Both these factors would eliminate the smectogenic tendencies as well as increase the N mesophase range

and the N-I transition temperature for compound **10** reported in the present investigation. These results are also in agreement with an earlier work²⁴. The difference in the molecular structure of both the compounds is only about the nature of terminal substituents on the terminal benzene nucleus. Probably the decrease in the polarizability of the compound **10** due to polar chloro group slightly overcomes the decreased molecular separation caused by the terminal substituent. Therefore, the width of the Cr-M as well as the N-I transition temperature of compound **10** becomes a little higher than that of compound A.

From the above discussion the order of terminal group efficiency for N phase thermal stability can be derived for the compounds as under



Experimental Section

Microanalysis of the compounds was performed on a Coleman carbon hydrogen analyzer at IIT Bombay. IR spectra were recorded in KBr pellets, on Shimadzu IR-408 spectrometer. ¹H NMR spectra were obtained in CDCl₃ on Jeol FX 300 MHz spectrometer using TMS as internal reference at CDRI, Lucknow. Liquid crystalline properties were investigated on a Leitz Laborlux 12 optical polarizing microscope provided with a heating stage at Applied Chemistry Department, MS University, Vadodara. The enthalpies of transition reported as J/g, were determined from DSC, obtained at scanning rate of 10°C/min, at Gharda Chemicals, Panoli. The calorimeter was

calibrated using pure Indium as standard. Mass spectra (EI) of the compound **10** was recorded at SAIF, IIT Madras, Chennai.

4-Hydroxybenzaldehyde, the appropriate *n*-alkyl bromide, α -naphthylamine, 2,4,5-trichloroaniline, NaNO_2 , K_2CO_3 , *etc.* were used as received. All solvents were dried and distilled prior to use.

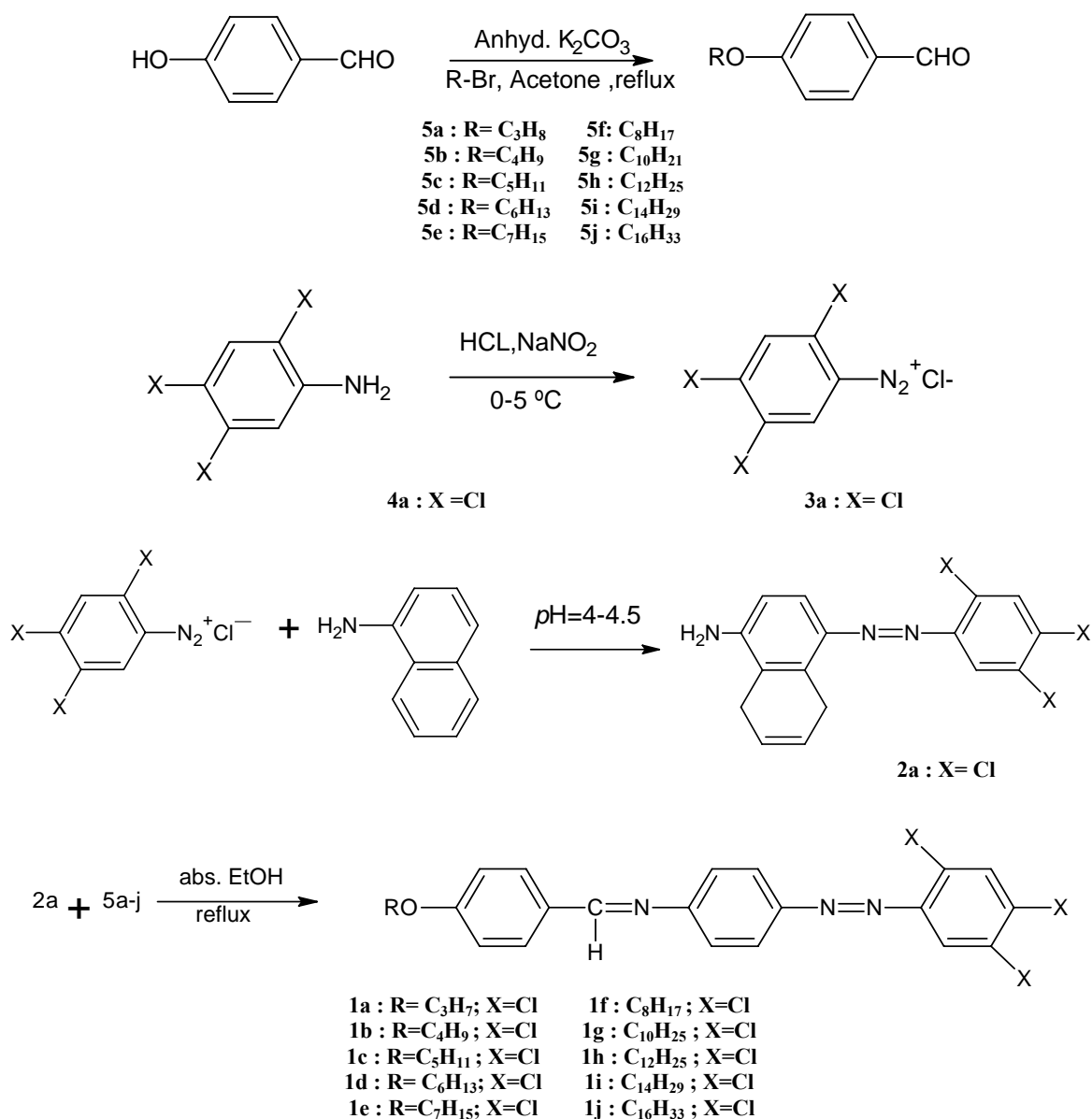
Synthesis

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

4-*n*-Alkoxybenzaldehyde, 5a-j

These were synthesized by the modified method of Gray and Jones²⁶.

4-Hydroxybenzaldehyde (0.1 mol, 12.2 g), anhydrous K_2CO_3 (0.15 mole, 20.85 g) and corresponding *n*-alkyl bromide (0.12 mol) were added to dry acetone (60 mL) in a round-bottom flask fitted with a reflux condenser. The reaction mixture was heated on a water bath for 8-12 hr. The whole mass was then poured into cold water and the aldehyde separated in the form of oily layer for lower members. The mass was extracted twice with ether. Ether extracts were combined and washed with dilute NaOH solution to remove unreacted 4-hydroxybenzaldehyde, followed by water and then dried. Ether was evaporated and the 4-*n*-alkoxybenzaldehyde thus obtained were purified by distillation under



Scheme I

reduced pressure. Boiling points (*n*-alkoxybenzaldehyde from C₂ to C₉ as 134, 141, 155, 163, 133, 143, 141, 163°C, respectively) agreed with those reported in literature²⁷.

(4-Aminonaphthalene-1-phenylazo)-2,4,5-trichlorobenzene, 2a

(4-Aminonaphthalene-1-phenylazo)-2,4,5-trichlorobenzene was synthesized by using conventional method of diazotization and coupling²⁸. The dye was purified by recrystallization from ethanol till constant melting point was obtained. Yield 78%, m.p. 195-196°C. Anal. Calcd. for C, 54.72; H, 2.85; N, 11.98. Found: C, 54.68; H, 2.82; N, 11.94%. ¹H NMR (CDCl₃): δ 6.82-8.15 (m, 8H, Ar) and 8.94-8.96 (d, 2H, NH₂).

4-[4'-*n*-Alkoxybenzylideneamino]-naphthalene-1-(2'', 4'', 5''-halo-1-azobenzene), 1a-j

To a stirred solution of the 4-aminonaphthalene 1-haloazobenzene (0.1 mol) in ethanol an appropriate alkoxyaldehyde (0.1 mol) was added, followed by 2-3 drops of acetic acid. The reaction mixture was refluxed for 2-3 hr. The orange precipitate was collected by filtration and washed with hot absolute ethanol. The crude products were purified by recrystallization several times from ethyl acetate until constant transition temperature were obtained. All the other compounds were obtained by the same method.

1g: An orange red crystalline solid; m.p. 205-06°C; Yield :76%; IR (KBr): 2878, 1623, 1603, 1441, 1399, 1234, 1166, 1049, 885 and 763 cm⁻¹; ¹H NMR (CDCl₃): δ 8.55 (s, 1H, 1×-CH=N-), 8.03-7.2 (m, 14H, Ar), 4.05 (t, 2H, 1× -OCH₂-), 1.87-1.46 (m, 8H, 4×-CH₂-) and 0.92 (t, 3H, 1×CH₃). Anal. Calcd. for C, 64.62; H, 4.82; N, 7.79. Found: C, 64.59; H, 4.79; N, 7.75%. EI-MS: *m/z* (%) 592 (M⁺-2).

Conclusion

A new mesogenic homologous series of naphthyl azomesogens with terminal multi-chloro groups was synthesized. The study indicated that the terminal multi-chloro group adversely affects mesophase thermal stability. However, due to the polar nature of

the chloro group, the effect is less pronounced compared to the terminal trichloro group.

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