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Study of homologous series of azomesogens with lateral chloro substitution

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ABSTRACT

A homologous series of azomesogens, 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo benzenes of twelve homologues has been synthesized. All the members of the series are either monotropically or enantiotropically nematogenic with threaded texture except first and second member of the series. Smectic mesophase does not occur by any derivatives of the series. Transition temperatures of solid-isotropic or solid-nematic follow zigzag path from first to seven member of the series. Rest of the homologues behaves in abnormal manner. The usual odd-even effect is observed in the nematic-isotropic (or vice versa) transition curve with alternation of transition temperature. Nematic-isotropic transitions do not behave in normal manner from and beyond eighth member of the series. Analytical data support the structure of the molecules. The mesomorphic properties of the series are compared with other structurally related homologous series. Titled homologous series is of middle ordered melting type.

Key words: Nematic, Monotropic, Mesomorphism, Azomesogens

INTRODUCTION

Liquid crystal substances are very important because of their many applications [1]. The increasing utility of liquid crystals (LC) materials in LC devices and in other fields of applications has inspired to plan the present investigation. A number of homologous series with –COO- and –N=N- central bridge have been synthesized by researcher [2-16].

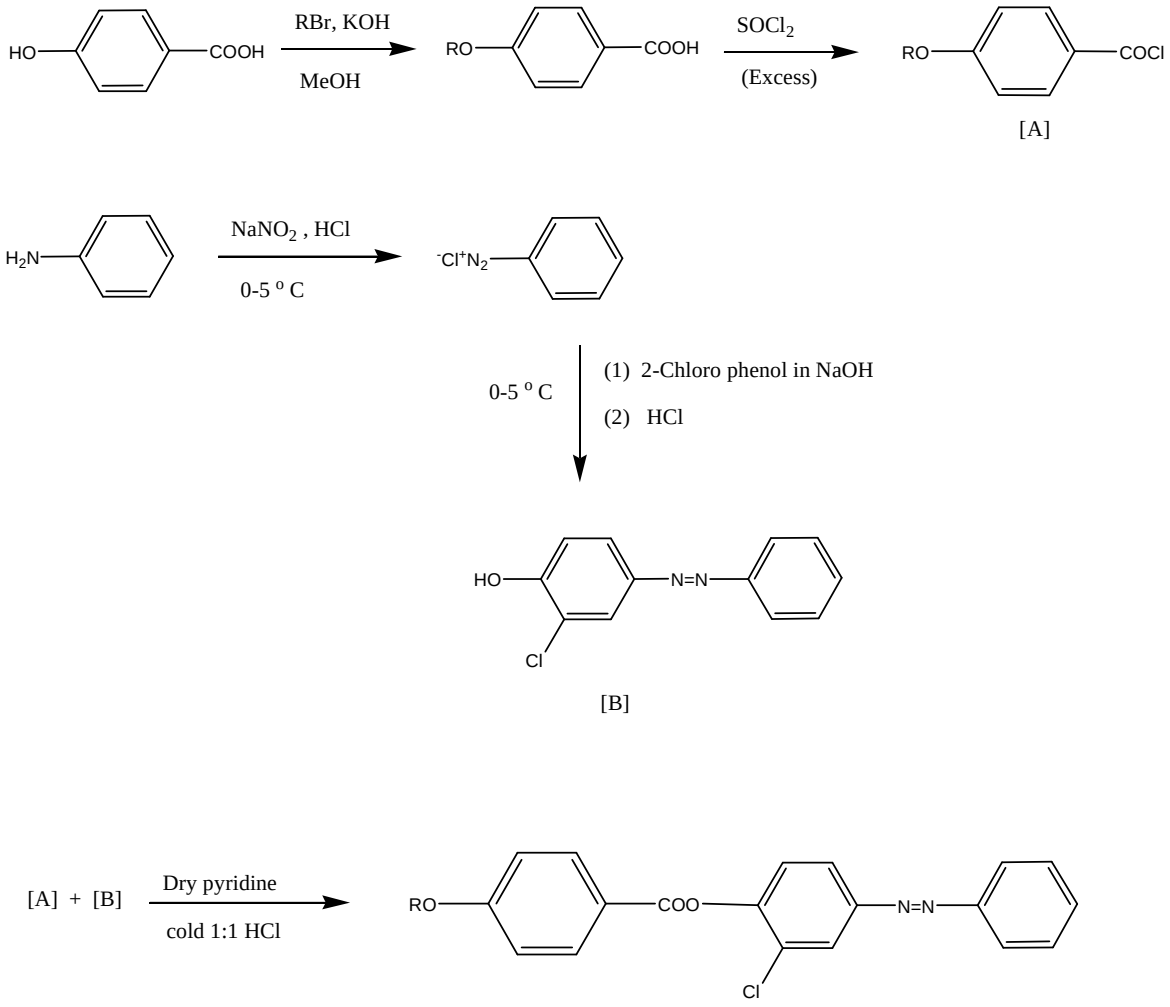
In the present study, a homologous series containing three phenyl rings in the main core linked through ester and azo central linkages and substituted by a lateral –Cl group on the middle phenyl ring has been synthesized and its mesomorphic properties compared with other similar homologous series.

MATERIALS AND METHODS

2-chloro phenol, aniline, sodium nitrate, pyridine, thionyl chloride, 4-hydroxy benzoic acid, n-alkyl halides were used directly as received. Solvents were dried and distilled before use.

Microanalysis of the compounds was performed on Perkin Elmer PE 2400 CHN Analyzer. IR spectra were recorded on Perkin Elmer Spectrum and ^{1}H NMR spectra were obtained with Bruker Spectrometer using $CDCl_3$ as solvent. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL Polarizing microscope with a heating stage. The synthetic route to the series-1 is illustrated in the **Scheme-I**.

4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides [A] were synthesized by the modified method of Dave and Vora [17]. 4-Hydroxy-3-chloro phenylazo benzene [B] was synthesized by using known method of diazotization and coupling [18]. 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo benzenes were synthesized by condensing 4-n-alkoxy benzoyl chlorides [A] with the 4-Hydroxy-3-chloro phenylazo benzene [B] in pyridine [19]. The azoesters were crystallized from alcohol till constant transition temperatures were obtained.



Where, R = -CnH_{2n+1}, n = 1 to 8, 10, 12, 14 & 16

Scheme-1 : Synthetic Route to Series-1 compounds

Transition temperatures are recorded in **Table-1.** The analytical data confirms the structure of molecules satisfactorily as under **Table-2.**

Table – 1: Transition temperatures for 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo benzenes

Sr. No.	R = n-alkyl chain	Transition temperature in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	140.0
2	Ethyl	-	-	145.0
3	Propyl	-	(81.0)	101.0
4	Butyl	-	(100.0)	110.0
5	Pentyl	-	81.0	89.0
6	Hexyl	-	84.0	95.0
7	Heptyl	-	54.0	81.0
8	Octyl	-	50.0	78.0
9	Decyl	-	55.0	82.0
10	Dodecyl	-	71.0	103.0
11	Tetradecyl	-	102.0	130.0
12	Hexadecyl	-	90.0	155.0

Value in parenthesis indicate monotropy

Table-2: Elemental analysis for 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenyl azo benzenes

Sr. No.	R = n-alkyl chain	Molecular Formula	Calculated %			Observed %		
			C	H	N	C	H	N
1	Methyl	$C_{20}H_{15}N_2O_3Cl$	65.48	4.09	7.64	65.36	4.01	7.69
2	Ethyl	$C_{21}H_{17}N_2O_3Cl$	66.23	4.47	7.36	66.29	4.44	7.29
3	Propyl	$C_{22}H_{19}N_2O_3Cl$	66.92	4.82	7.10	66.99	4.89	7.18
4	Butyl	$C_{23}H_{21}N_2O_3Cl$	67.56	5.14	6.85	67.47	5.19	6.89
5	Pentyl	$C_{24}H_{23}N_2O_3Cl$	68.16	5.44	6.63	68.25	5.48	6.55
6	Hexyl	$C_{25}H_{25}N_2O_3Cl$	68.73	5.73	6.41	68.78	5.69	6.49
7	Heptyl	$C_{26}H_{27}N_2O_3Cl$	69.26	5.99	6.21	69.19	5.90	6.28
8	Octyl	$C_{27}H_{29}N_2O_3Cl$	69.75	6.24	6.03	69.83	6.28	6.13
9	Decyl	$C_{29}H_{33}N_2O_3Cl$	70.66	6.70	5.68	70.60	6.79	5.60
10	Dodecyl	$C_{31}H_{37}N_2O_3Cl$	71.47	7.11	5.38	71.41	7.10	5.32
11	Tetradecyl	$C_{33}H_{41}N_2O_3Cl$	72.20	7.47	5.10	72.29	7.36	5.19
12	Hexadecyl	$C_{35}H_{45}N_2O_3Cl$	72.85	7.80	4.86	72.88	7.77	4.82

IR Spectrum for n-Propyloxy Derivative (v_{max}/cm^{-1}): 2926, 2842, 1457.1, 1383.8 (-C-H, aliphatic), 1730, 1261.4 (ester group), 1601.8 (-N=N- group), 1559.3 (-C=C-, aromatic), 1053.1 (ether group), 846.7 (p- sub. benzene ring), 761.8 (tri sub. benzene ring), 1021.2 (C-Cl aromatic).

IR Spectrum for n-Dodecyloxy Derivative (v_{max}/cm^{-1}): 2926, 2852, 1466.8, 1351 (-C-H, aliphatic), 1732, 1257 (ester group), 1599 (-N=N- group), 1574.3 (-C=C-, aromatic), 1063 (ether group), 831.3 (p- sub. benzene ring), 759.9 (tri sub. benzene ring), 1043.4 (C-Cl aromatic).

^{1}H NMR ($CDCl_3$, Standard TMS) for Methoxy Derivative (δ ppm): 3.91 (s, 3H, -OCH_3), 7.04 (d, 2H, Ar-H), 7.44-8.07 (m, 8H, Ar-H), 8.23 (d, 2H, Ar-H)

^{1}H NMR ($CDCl_3$, Standard TMS) for n-Pentyloxy Derivative (δ ppm): 0.95 (t, 3H, -CH_3), 1.31-1.54 (m, 4H, 2X, -CH_2-), 1.84 (m, 2H, -OCH_2-$\underline{C}H_2$-) , 4.05 (t, 2H, -OCH_2-), 7.02 (d, 2H , Ar-H), 7.43-7.95 (m, 8H, Ar-H), 8.17 (d, 2H, Ar-H)

RESULTS AND DISCUSSION

Twelve homologous of the series, 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo benzenes were synthesized and their mesomorphic properties are studied. The transition temperatures of the homologous series are recorded in **Table-2.** The first two homologues are non-mesomorphic in nature. Mesomorphism commences from third homologue and ends to last homologue. Propyl and Butyl derivatives exhibited nematic mesophase in the Monotropic behavior while from and beyond the pentyl derivative it exhibit enantiotropic nematic behavior till hexadecyl derivative. This series is entirely nematogenic. Smectic mesophase is absent even in the Monotropic condition.

The transition temperatures are plotted versus the number of carbon atoms is n-alkyl chain of lift n-alkoxy group of the homologues. The phase diagram is represented in **Figure-1**. The solid-mesomorphic or solid-isotropic transition curve follows a zigzag path of rising and falling tendency up to seventh member of the series and falls to the eighth homologue. Thereafter it rises continuously up to the fourteenth homologue, and finally falls off at the sixteenth homologue. The nematic-isotropic or vice-versa transition curve for even member follows smooth gradual falling up to the eighth homologue.

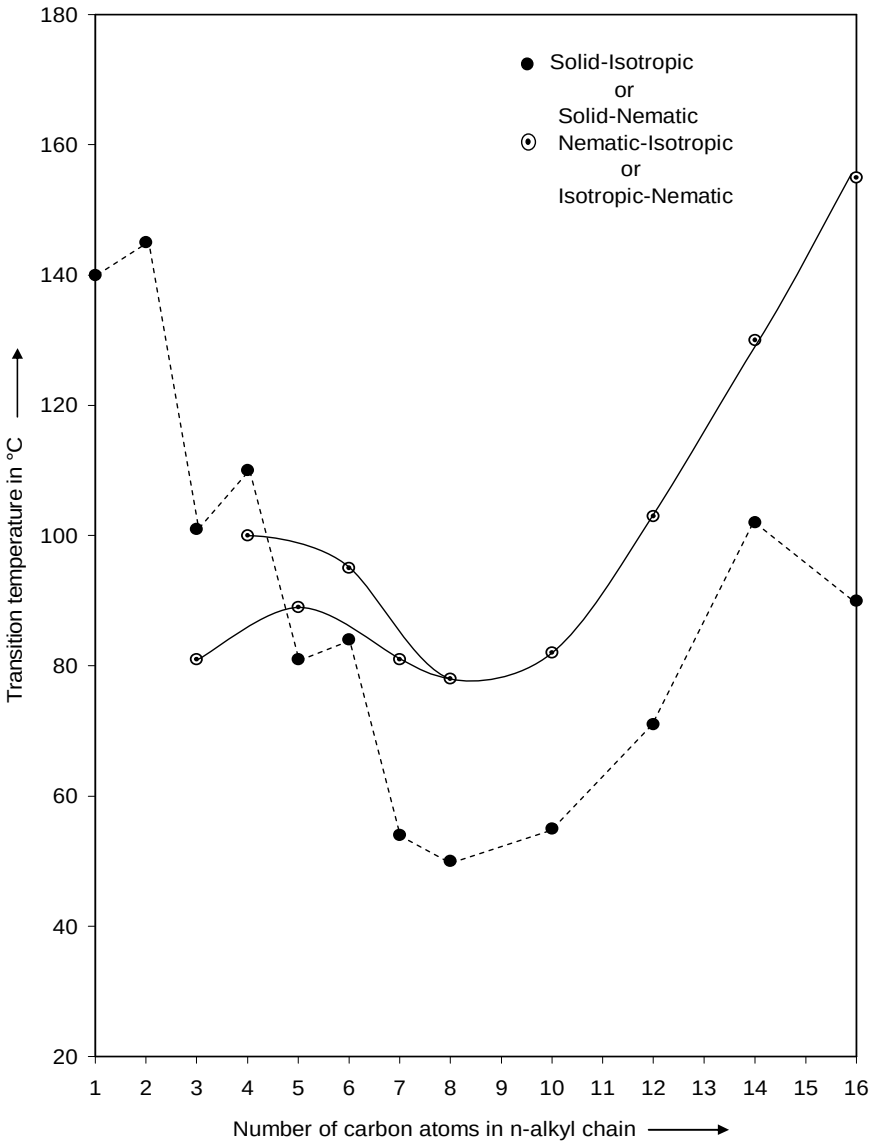
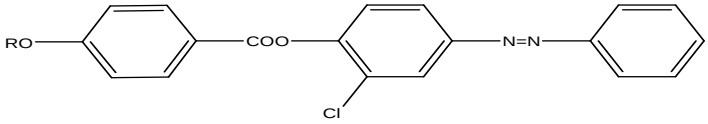
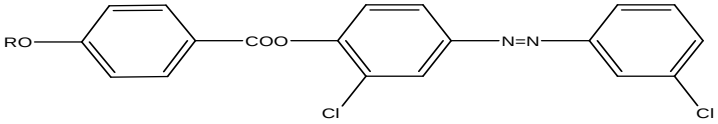


Fig. 1 : 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo benzenes

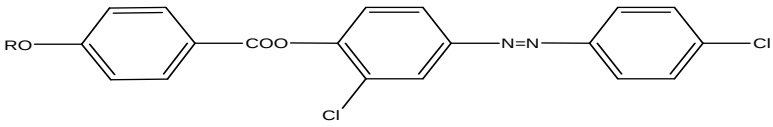
[1] 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenyl azo benzenes



[A] 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenyl azo-3''-chlorobenzenes [20]



[B] 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenyl azo-4''-chlorobenzenes [21]



Where, R = $-C_nH_{2n+1}$, n = 1 to 8, 10, 12, 14 & 16.

Figure - 2: Relative Characteristic of series

Thereafter rising continues up to last member of the series. While odd members of the series, transition curve rises from the third to the fifth and slowly falls to the seventh and then merges at the eighth homologue to the main stream of nematic-isotropic or vice-versa transition curve. Thus odd-even effect is observed and then curve follow unusual path of rising. The nematic-isotropic (or vice-versa) transitions are between 78 °C and 155 °C with mesophase range varying from minimum of 8.0°C at the fifth homologue to maximum of 65°C at sixteenth homologue. Thus, homologue series under present investigation is middle ordered melting type. Non-mesomorphic behavior of the first two homologues is due to their high crystallizing tendency arising out of their strong intermolecular attractions as compared to other members of the same series as a consequence of shorter n-alkoxy terminal group viz. $–OCH_3$ and $–OC_2H_5$ linked on left side of the molecules. First and second homologues of the series pass directly from solid to isotropic state without exhibition of mesomorphic state because molecules of methyl and ethyl derivatives are unable to resist thermal vibration and transform into isotropic liquid relatively at higher temperature. Propyl and butyl derivatives are Monotropic nematic and pentyl to hexadecyl derivatives are enantiotropic nematic. Thus entire series is nematogenic without exhibition of smectogenic character even in the Monotropic condition. Thus, statistically parallel orientation order of molecules is maintained resisting thermal vibrations due to end to end attraction even in the floating condition from propyl to hexadecyl derivatives. From phase diagram **(figure-1)** it is seen that, solid-isotropic or solid-nematic transition curve follows zigzag path of rising and falling behaves in normal manner with exception at eighth and twelfth homologue. Nematic-isotropic (or vice-versa) transition curve initially falls and than rises as series is ascended because of the presence of laterally substituted polarizable chloro group at the middle phenyl ring. Smectic mesophase is totally absent for all members of the titled homologous series because of the extent of non co-planarity caused by the molecules which resulted intermolecular force of attractions in such a manner that molecules are incapable to maintain layered arrangement of the molecules even in the monotropic condition till the last homologue of the series. Odd-even effect is observed for

nematic-isotropic transition curve but it diminishes as series is ascended from and beyond eighth homologues because higher homologues are of even numbered and in case of higher homologues, the longer left n-alkyl chain of n-alkoxy group may coiled and bend or coupled to lie in the line with major axis of the core. Thus end to end contact would then ultimately be the same for odd and even homologue. The mesomorphic characteristics of the title homologous series-1 are compared with structurally similar homologous series-A & B **(figure-2).** The homologous series-1, A & B posses three phenyl rings. Linked through –COO- and –N=N- central bridges, left n-alkoxy terminal group at the para position with chloro group at ortho position to –COO- unit at middle phenyl ring as common identical features, while they differ only by right functional groups substituted at third phenyl ring. The variation in the mesomorphic characteristics can be attributed to the presence of different terminal groups which have different polarity and polarizability for the formation of mesophase.

The average thermal stability of present homologous series-1, A & B are given in **Table-3**. Nematic-isotropic average thermal stability of homologous series-B is the highest amongst the series under comparison. Relatively the highest polarity and polarizability of terminally attached –Cl functional group with respect to –Cl (meta) and –H raised the intermolecular forces of attractions and hence resulting into highest nematic-isotropic thermal stability.

Table-3: Average Thermal Stabilities in °C

Series	1	A	B
Smectic-Isotropic or Smectic-Nematic	-	-	75.75 (C10-C16)
Commencement of Smectic phase	-	-	C_{10}
Nematic-Isotropic or Isotropic-Nematic	102.0 (C_3-C16)	130.6 (C6-C14)	149.4 (C3-C16)
Commencement of Nematic phase	C3	C6	C3

This reflects the relative nematic-isotropic thermal stabilities of series. Thus, from the above discussion, the terminal group efficiency order from the nematic-isotropic thermal stability can be derived as under.

Nematic group efficiency order for terminal substitution:-Cl (para) > -Cl (meta) > -H

Smectic group efficiency order for terminal substitution:-Cl (para) > -Cl (meta) & -H

CONCLUSION

A new mesogenic homologous series with laterally substituted chloro group on the middle phenyl ring has been synthesized for the study of mesomorphic characteristics. All the members of the series exhibit nematic phase under monotropic or enantiotropic condition except the first two homologues, with absence of Smectic property. The average thermal stability of present homologous series-1 is lower than those of structurally related compounds. This can be due to the presence of –H as the terminal atom.

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