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Synthesis and Characterization of Azoester Mesogens and Study of the Effect of Lateral substituent on Their Mesomorphic Properties

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ABSTRACT

Mesogenic homologous series, 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4''-chlorobenzenes of twelve homologues has been synthesized. The first three and last three member of the series is non–mesomorphic. Mesomorphism commences from fourth homologue and ends to tenth homologue. Fourth to tenth homologues are monotropic nematic, while sixth homologue is enantiotropic nematic. Thus, totally six members of the titled homologous series are monotropically or enantiotropically nematogenic with threaded type texture. Smectic mesophase does not occur in any homologue of the series even in the monotropic condition. The solid-isotropic or solid-nematic transition curve follows a zigzag path of rising and falling tendency as series is ascended. The usual odd-even effect is observed in the nematic-isotropic (or vice versa) transition curve with alternation of transition temperature. Transition temperatures are observed through polarizing microscope with heating stage. The average thermal stabilities and mesomorphic properties of the series are compared with structurally similar other homologous series. Analytical data support the structure of the molecules.

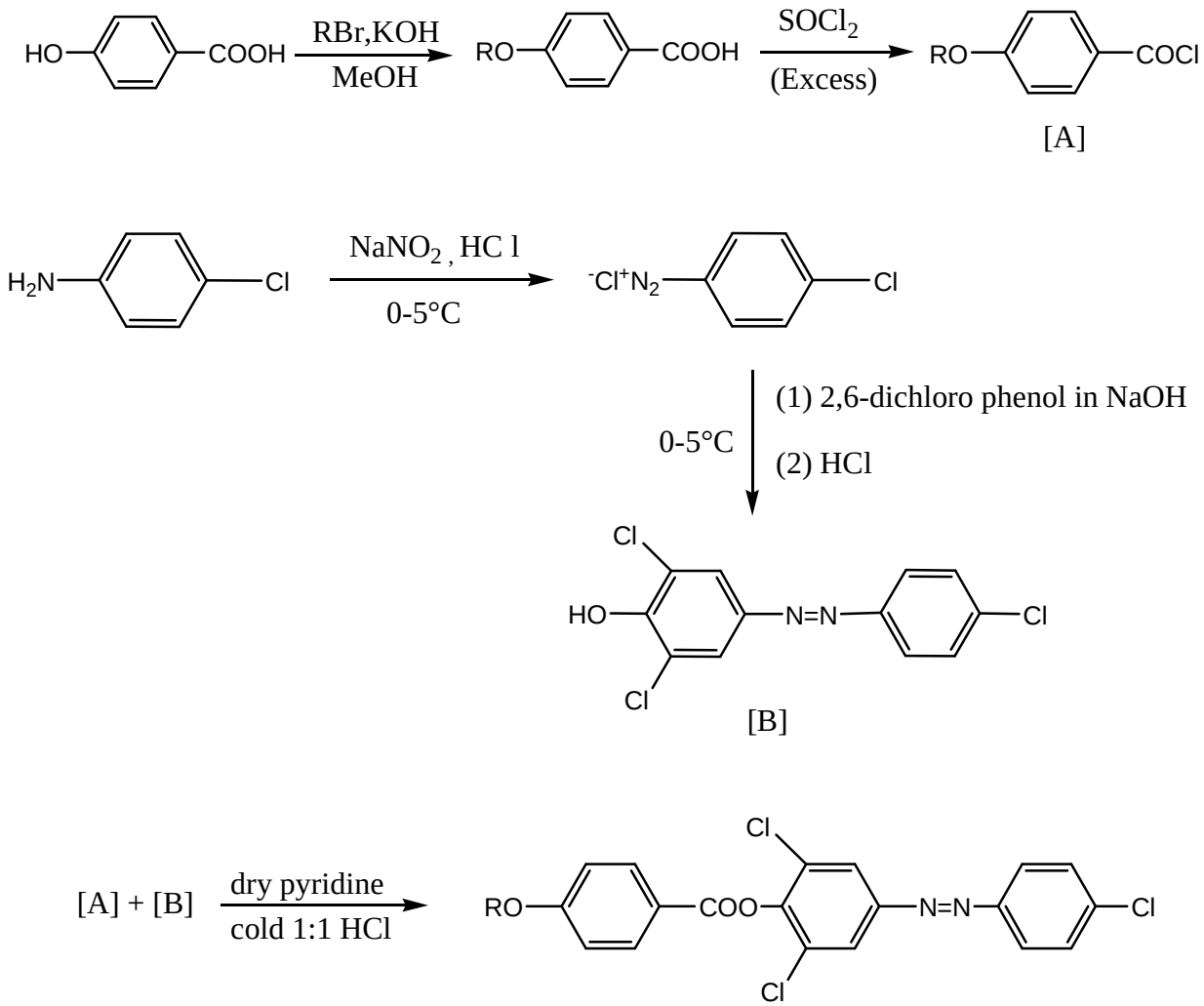
Keywords: Nematic, Monotropic, Mesomorphism, Smectic.

INTRODUCTION

The thermotropic liquid crystals have found extensive applications in medical field, analysis of chemicals, drugs etc. The increasing utility of liquid crystal material in electronic display devices and in many other fields of applications inspired to plan the present investigation. A number of homologous series with –COO- and –N=N- central bridge have been synthesized by researchers [1-14]. In the present study, a homologous series containing three phenyl rings in the main core linked through central linkages as well as left and right n-alkoxy and chloro terminals respectively and laterally substituted middle phenyl ring by two chloro groups has been synthesized in order to study of their effect on mesomorphic properties.

MATERIALS AND METHODS

4-hydroxy benzoic acid, the appropriate n-alkyl bromides, 2, 6-dichloro phenol, 4-chloro aniline, sodium nitrate, pyridine, thionyl chloride were used directly as received. Solvents were dried and distilled before use. Microanalysis of the compound 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 series-1 is illustrated in the **scheme-1**.



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

Scheme-1 : Synthetic Route to series-1 compounds

(1) 4-n-alkoxy benzoic acids and corresponding 4-n-alkoxy benzoyl chlorides [A] were synthesized by the modified method of Dave et al [15].
(2) 4-hydroxy-3,5-dichloro phenylazo-4'-chlorobenzene [B] was prepared by known method of diazotization and coupling [16].

(3) 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4''-chlorobenzenes were synthesized by adding drop wise a solution of 4-hydroxy-3,5-dichloro phenylazo-4'-chlorobenzene in pyridine to an ice cooled solution respective 4-n-alkoxy benzoyl chloride with constant stirring. The reaction mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 cold aqueous hydrochloric acid and final products were obtained by subsequent usual steps. The resulting products were crystallized from alcohol till constant transition temperatures were obtained.

The transition temperatures are recorded in **Table-1**. The elemental analysis of all compounds of series-1 was found satisfactory and mentioned in **Table-2.**

Table 1: Elemental analysis for 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4"-chlorobenzenes

Sr. No.	R = n-alkyl chain	Molecular Formula	Calculated %			Observed %		
			C	H	N	C	H	N
1	Methyl	$C_{20}H_{13}N_2O_3Cl_3$	55.11	2.98	6.43	55.18	2.87	6.49
2	Ethyl	$C_{21}H_{15}N_2O_3Cl_3$	56.06	3.34	6.23	56.16	3.27	6.27
3	Propyl	$C_{22}H_{17}N_2O_3Cl_3$	56.96	3.67	6.04	56.85	3.56	6.10
4	Butyl	$C_{23}H_{19}N_2O_3Cl_3$	57.80	3.98	5.86	57.88	3.85	5.92
5	Pentyl	$C_{24}H_{21}N_2O_3Cl_3$	58.60	4.27	5.70	58.67	4.35	5.75
6	Hexyl	$C_{25}H_{23}N_2O_3Cl_3$	59.35	4.55	5.54	59.44	4.50	5.59
7	Heptyl	$C_{26}H_{25}N_2O_3Cl_3$	60.06	4.81	5.39	60.14	4.76	5.47
8	Octyl	$C_{27}H_{27}N_2O_3Cl_3$	60.73	5.06	5.25	60.94	5.18	5.29
9	Decyl	$C_{29}H_{31}N_2O_3Cl_3$	61.98	5.52	4.99	61.86	5.43	4.87
10	Dodecyl	$C_{31}H_{35}N_2O_3Cl_3$	63.10	5.94	4.75	63.19	5.98	4.70
11	Tetradecyl	$C_{33}H_{39}N_2O_3Cl_3$	64.13	6.31	4.53	64.22	6.38	4.59
12	Hexadecyl	$C_{35}H_{43}N_2O_3Cl_3$	65.06	6.66	4.34	65.17	6.56	4.29

IR for n-hexyloxy derivative (cm^{-1}): 3063 (-CH aromatic stre.), 2950, 2860, 1444.6,1394 (alkyl group), 1743.5, 1239.2 (-COO- group), 1608 (-N=N- group), 1575.7 (-C=C- aromatic stre.), 1086.8 (-O- group), 839.9 (p-sub. benzene ring), 1042 (C-Cl aromatic).

IR for n-octyloxy derivative (cm^{-1}): 3052 (-CH aromatic stre.), 2948, 2856, 1473, 1350.1 (alkyl group), 1734.9, 1239.2 (-COO- group), 1608 (-N=N- group), 1576.7 (-C=C- aromatic stre.), 1087.8 (-O- group), 838 (p-sub. benzene ring), 1033.8 (C-Cl aromatic).

^1H NMR ($CDCl_3$, std. TMS) for n-propyloxy derivative (δppm): 1.05 (t, 3H, $-CH_3$), 1.85 (m, 2H, $-OCH_2-\underline{CH_2}-$), 4.02 (t, 2H,$-OCH_2-$), 6.91 (d, 2H, Ar-H), 7.49 (d, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.90 (s, 2H, Ar-H), 8.19 (d, 2H, Ar-H).

^1H NMR ($CDCl_3$, std. TMS) for n-butyloxy derivative (δppm): 1.0 (t, 3H, $-CH_3$), 1.58 (m, 2H, $-CH_2-$), 1.86 (m, 2H, $-OCH_2-\underline{CH_2}-$), 4.07 (t, 2H,$-OCH_2-$), 7.03 (d, 2H, Ar-H), 7.53 (d, 2H, Ar-H), 7.86 (d, 2H, Ar-H), 7.98 (s, 2H, Ar-H), 8.18 (d, 2H, Ar-H).

Table – 2: Transition temperatures for 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4"- chloro benzenes

Sr. No.	R = n-alkyl chain	Transition temperature in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	144.0
2	Ethyl	-	-	164.0
3	Propyl	-	-	171.0
4	Butyl	-	(114.0)	130.0
5	Pentyl	-	(88.0)	120.0
6	Hexyl	-	96.0	117.0
7	Heptyl	-	(88.0)	90.0
8	Octyl	-	(103.0)	106.0
9	Decyl	-	(68.0)	73.0
10	Dodecyl	-	-	70.0
11	Tetradecyl	-	-	79.0
12	Hexadecyl	-	-	70.0

Value in parenthesis indicate monotropy

RESULTS AND DISCUSSION

4-hydroxy-3,5-dichloro phenylazo-4'-chlorobenzene is a non-liquid crystal compound but linking of phenyl ring bridged through –COO- and left n-alkoxy terminal increases the length of the molecules enhancing lateral intermolecular attractions and polarizability. Homologous series 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4''-chlorobenzenes are nematogenic in nature. The first three and last three members of the series do not display any kind of mesomorphic property. Mesomorphism is displayed by fourth to tenth members of the series in monotropic nematic manner except sixth homologue of the series which displays enantiotropically nematic. Thus, totally six members of the title homologous series are mesomorphic in nature. Smectic mesophase is absent even in the monotropic condition.

The transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy group of the homologous series. The phase diagram is represented in **figure-1**. The solid-isotropic or solid-nematic transition curve follows zigzag path of rising and falling tendency as observed normally in case of homologous series. In case of first to third homologue, it rises steeply and then continuously falls up to seventh member of the series and again rises at eighth member of the series with fall up to twelfth member and again rises at fourteenth member of the series. Then again it falls up to the last member of the homologous series by 9.0°C. Zigzag path of solid-isotropic or solid-nematic curve is due to the sequential addition of methylene unit at the left n-alkoxy group. This causes differences in the length and linearity of the molecules and hence the difference in end to end intermolecular forces of attractions. It is directly related to magnitude of cohesive forces arising out of odd and even number of carbon atoms in n-alkoxy terminal. Thus, overall end to end intermolecular forces of attractions are altered from homologue to homologue in the same series for odd and even member of the series. The odd-even effect is observed in the nematic-isotropic (or vice versa) transition curve with alternation of transition temperature. Thus, nematic-isotropic (or vice versa) transition curve behaves in normal manner from fourth to tenth homologues of the series. The nematic mesophase appeared

has threaded type of texture as judged directly by observing the sample of a homologue in a field of view of the hot stage polarizing microscope.

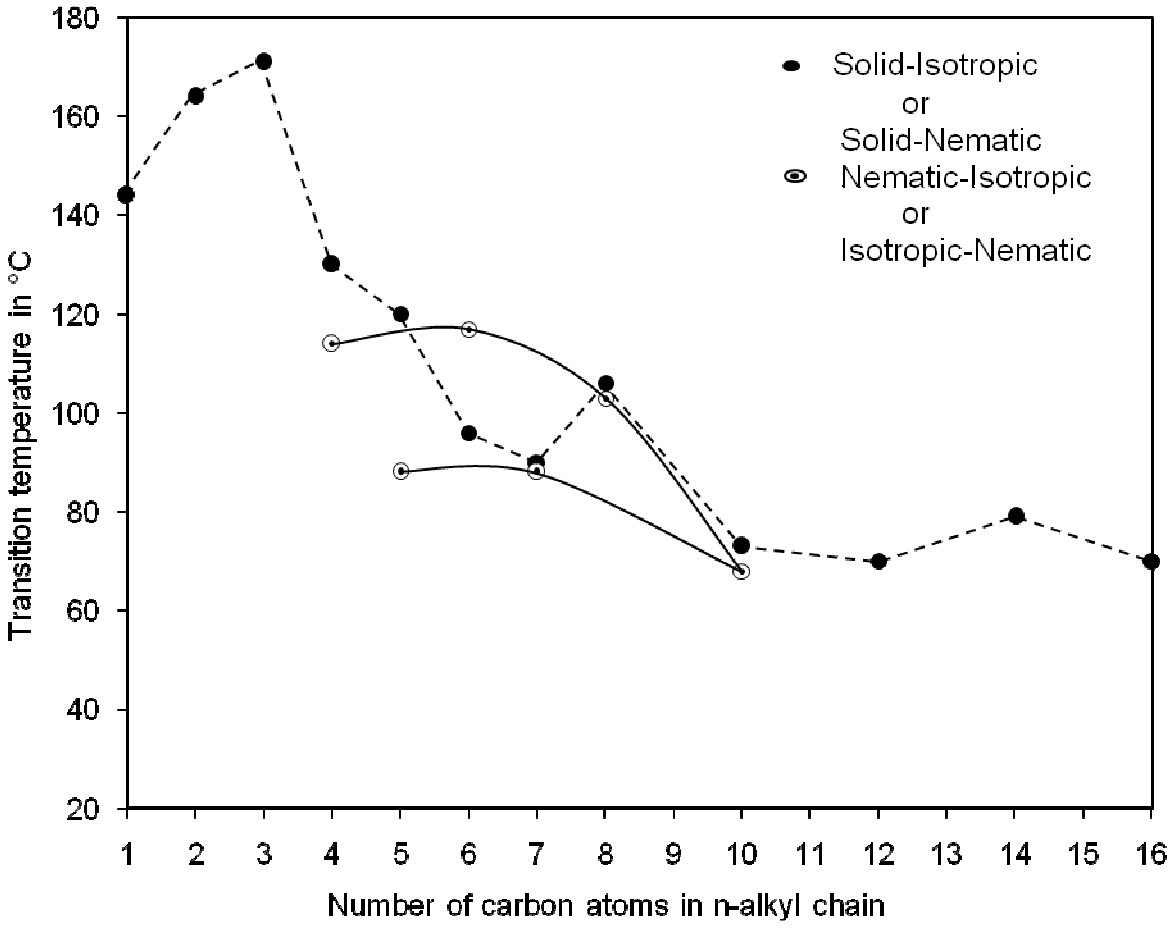
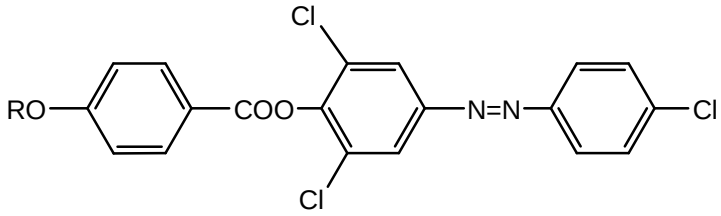


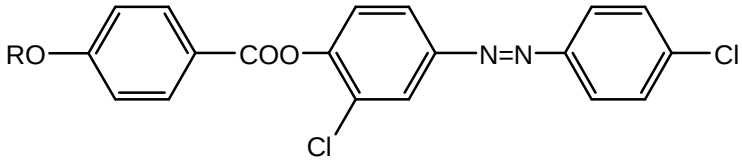
Figure-1: The phase behavior of the series

First three and last three member of the homologous series are non-mesogenic because of their high crystallizing tendency and the incapability of intermolecular cohesion force to maintain statistically parallel orientation at order of molecules in floating condition or to form ordered sliding layered arrangement of molecules with lamellar packing in floating condition. Enantiotropic/monotropic nematic property is exhibited by the remaining members of the series due to the statistically parallel orientation of molecules with end to end attraction in floating condition resisting thermal vibrations. Absence of smectic mesophase is attributed to insufficient intermolecular forces of attraction to form sliding layered arrangement of molecules in the crystal structure. Appearance of odd-even effect and alternation of transition temperature is attributed to the linking of number of methylene units through oxygen atom as n-alkoxy group. It is seen that nematic-isotropic (or vice versa) transition curve shows alternation of transition temperatures from fourth to the tenth homologue. The mesomorphic characteristics of the title homologous series-1 are compared with structurally similar other homologous series- A & B (figure-2).

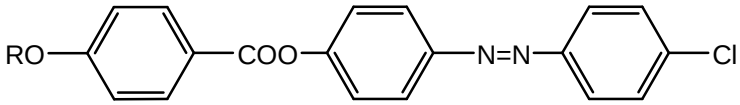
(1) 4-(4'-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4''-chlorobenzenes



(A) 4-(4'-n-alkoxy benzoyloxy)-3-chloro phenylazo-4''-chlorobenzenes [13]



(B) 4-(4'-n-alkoxy benzoyloxy)- phenylazo-4''-chlorobenzenes [14]



where, R=-CnH2n+1, n= 1 to 8, 10, 12, 14 & 16

Figure-2

The homologous series-1, A & B possess three phenyl rings linked through –COO- and –N=N- central bridge, left n-alkoxy terminal group at para position as well as right chloro end group as common identical moiety, while they differ only by functional groups substituted in middle phenyl ring. Hence the variation in mesomorphic characteristics and degree of mesomorphism is varied due to the varied substituted middle phenyl ring. The laterally substituted chloro groups at the middle phenyl ring increases intermolecular distance. Consequently intermolecular attraction may diminish. However, lateral substitution increases the width of molecule and affect to the length to breadth ratio and increases polarizability which can increase intermolecular forces of attractions of molecules. Thus, on increasing widths of a molecule two opposing effects are operating at a time. The net effect will depend up on the predominance of two opposing effects. Therefore mesomorphic characteristics of a molecule depend up on magnitude of net resultant adhering force of attractions. Smectic mesophase is totally absent in case of series-1, because steric hindrance caused by 3,5-dichloro group as compared to –H and –Cl in case of series (A) and (B) which keep molecules more aparted reducing intermolecular forces of attractions.

The average thermal stabilities of present homologous series-1, A and B are given in **Table-3.** The average thermal stabilities of series-B is the highest among the series under comparison because molecules of series-B are long linear without any substitution (other than –H) at lateral position.

Table-3: Average Thermal Stabilities in °C

Series	1	A	B
Smectic-Isotropic or Smectic-Nematic	-	75.75 (C_{10}-C_{16})	148.7 (C_6-C_{16})
Commencement of smectic phase	-	C_{10}	C_6
Nematic-Isotropic or Isotropic-Nematic	106.0 (C_4-C_{10})	149.4 (C_3-C_{16})	217.6 (C_1-C_{10})
Commencement of nematic phase	C_4	C_3	C_1

This causes to keep relatively closest approach of molecules resulting into highest magnitude of intermolecular attractions. Thus, it exhibits smectic and nematogenic behavior with highest thermal stability. Nematic-isotropic average thermal stability of series-1 is lower than series-A & B. The molecular structure of series-1 differs from series-A & B only at middle aromatic core, i.e. series-1 has lateral 3,5-dichloro group attached at the middle phenyl ring, whereas series-A & B have -Cl and –H lateral substituent at similar phenyl ring respectively. Thus, as compared to series-B, series-A & series-1 have increased breadth due to the laterally substituted 3,5-dichloro and –Cl group. Gray [17] has explained that increase in the breadth of the molecules reduces both nematic and smectic mesophase stability. Thus, Gray's view is supported by present investigation. It seems that, the lateral 3,5-dichloro and –Cl group not only increase the breadth of the molecules of series-1 and series-A but also affects considerably the non-coplanarity in the system due to steric interaction. Both these factors would eliminate the smectogenic property from title homologous series-1 under present investigation. Thus, from the above discussion the lateral group efficiency order from the nematic-isotropic and smectic-nematic thermal stability can be derived as under.

Nematic group efficiency order (lateral substitution): -H > -Cl > 3, 5-dichloro
Smectic group efficiency order (lateral substitution): -H > -Cl > 3, 5-dichloro

CONCLUSIONS

A new homologous series with laterally substituted 3,5-dichloro group on middle phenyl ring has been synthesized for the study of their mesomorphic properties. The study indicated that the lateral two chloro groups adversely affect the mesophase thermal stabilities. Laterally substituted two groups do not allow formation of smectic mesophase even in the monotropic condition.

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