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### Synthesis and Study of New Mesogenic Homologous Series: 4-(4'-n-alkoxy benzoyloxy)-3, 5-dichloro phenylazo-4''-methyl benzenes

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#### ABSTRACT

A homologous series of azoester mesogens, 4-(4'-n-alkoxy benzoyloxy)-3, 5-dichloro phenylazo-4''-methyl benzenes of twelve homologues has been synthesized. The first three and last two member of the series is non-mesomorphic. Mesomorphism commences from fourth homologue and ends to twelfth homologue. Fifth to tenth homologues are enantiotropic nematic, while fourth and twelfth homologue is monotropic nematic. Thus, totally seven member of the titled homologous series are mesomorphic in nature. Smectic mesophase does not occur in any homologue of the series even in the monotropic condition. The usual odd-even effect is observed in nematic-isotropic transition curve. The average thermal stability and liquid crystalline properties are compared with structurally identical homologous series. Analytical data support the structures of molecules. Transition temperatures of homologues are observed through hot stage polarizing microscope. Texture of the homologues is of threaded type nematogens.

**Key words:** Mesomorphism, Nematic, Liquid crystal, Monotropic.

#### INTRODUCTION

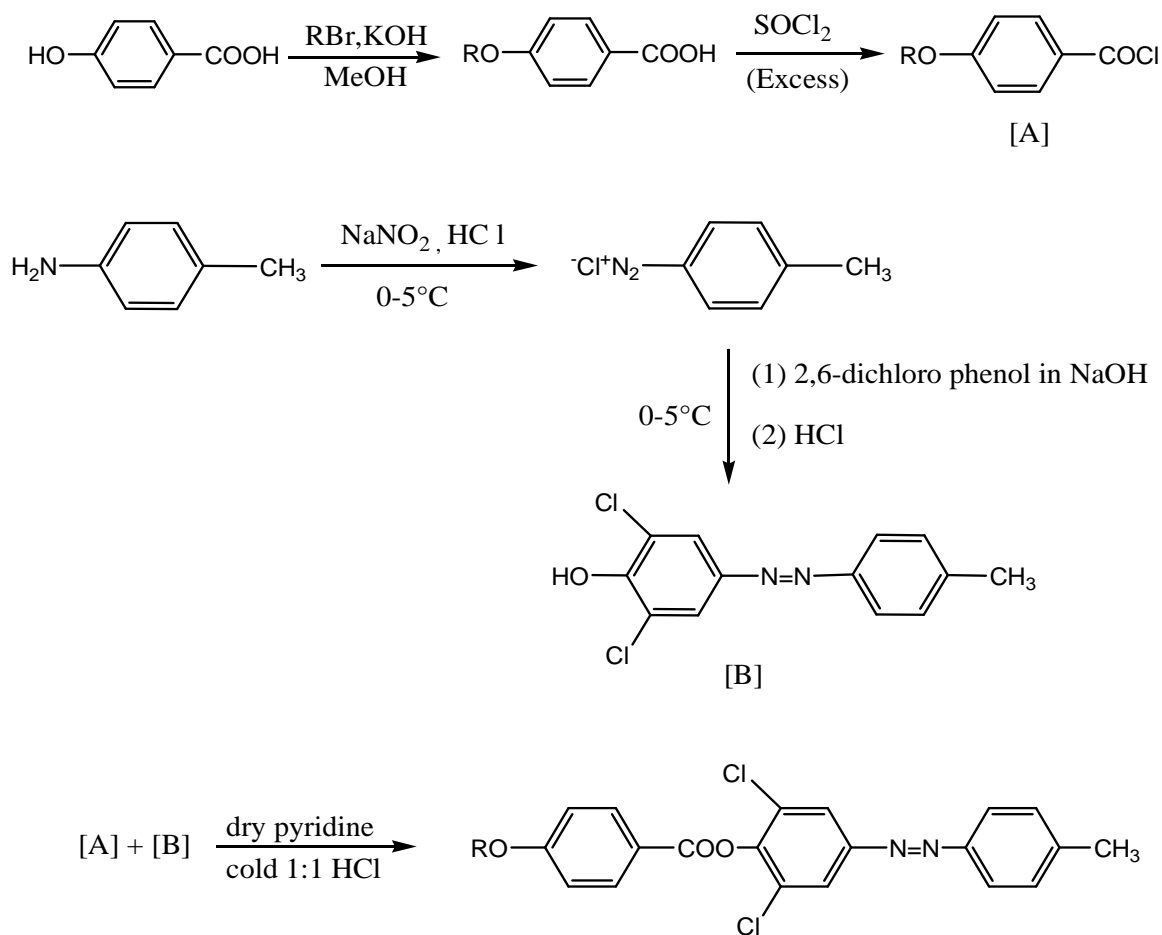
A number of homologous series which have rod like linear molecular structures were synthesized by researchers [1-5]. Presently, we have synthesized a new homologous series comprising of azoester central linkages and laterally substituted middle phenyl ring by two chloro groups.

#### MATERIALS AND METHODS

2, 6-dichloro phenol, 4-amino toluene, 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  $^1\text{H}$  NMR Spectra were obtained with a Bruker spectrometer using  $\text{CDCl}_3$  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**.

4-n-alkoxy benzoic acid and corresponding 4-n-alkoxy benzoyl chlorides [A] were synthesized by the modified method of Dave et al [6]. 4-hydroxy-3, 5-dichloro phenylazo-4'-methyl benzene [B] was prepared by known method [7]. The azodye [B] formed was filtered, washed with water, dried and crystallized in glacial acetic acid several times. The yield is about 68.8%, m.p.  $119.0^\circ\text{C}$ . 4-(4'-n-alkoxy benzoyloxy)-3, 5-dichloro phenylazo-4''-methyl benzenes were synthesized by usual established method [8].



Where,  $\text{R} = -\text{C}_n\text{H}_{2n+1}$ ,  $n = 1$  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, 5-dichloro Phenylazo-4''-methyl benzenes**

Sr. No.	R = n-alkyl chain	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	191.0
2	Ethyl	-	-	185.0
3	Propyl	-	-	184.0
4	Butyl	-	(140.0)	150.0
5	Pentyl	-	106.0	126.0
6	Hexyl	-	75.0	122.0
7	Heptyl	-	88.0	103.0
8	Octyl	-	79.0	96.0
9	Decyl	-	78.0	109.0
10	Dodecyl	-	(85.0)	88.0
11	Tetradecyl	-	-	114.0
12	Hexadecyl	-	-	123.0

*Value in parenthesis indicate monotropy*

**Table -2: Elemental analysis for 4-(4'-n-alkoxy benzoyloxy)-3, 5-dichloro phenylazo-4''-methylbenzenes**

Serial No.	R = n-alkyl chain	Molecular Formula	Calculated %			Observed %		
			C	H	N	C	H	N
1.	Methyl	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	60.72	3.85	6.75	60.69	3.90	6.88
2.	Ethyl	C <sub>22</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	61.54	4.19	6.53	61.45	4.25	6.45
3.	Propyl	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	62.30	4.51	6.32	62.35	4.42	6.38
4.	Butyl	C <sub>24</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	63.02	4.81	6.12	63.10	4.75	6.20
5.	Pentyl	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	63.69	5.09	5.94	63.60	5.16	5.83
6.	Hexyl	C <sub>26</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	64.33	5.36	5.77	64.35	5.25	5.70
7.	Heptyl	C <sub>27</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	64.93	5.61	5.61	64.89	5.76	5.55
8.	Octyl	C <sub>28</sub> H <sub>30</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	65.49	5.85	5.46	65.55	5.80	5.40
9.	Decyl	C <sub>30</sub> H <sub>34</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	66.54	6.28	5.17	66.60	6.35	5.25
10.	Dodecyl	C <sub>32</sub> H <sub>38</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	67.49	6.98	4.92	67.57	6.60	4.82
11.	Tetradecyl	C <sub>34</sub> H <sub>42</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	68.34	7.03	4.69	68.44	7.13	4.60
12.	Hexadecyl	C <sub>36</sub> H <sub>46</sub> N <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	69.12	7.36	4.48	69.20	7.29	4.52

**IR Spectrum for n-propyloxy Derivative:**  $\nu_{\max}$  /cm<sup>-1</sup> : 3060 (-C-H aromatic stre.), 2960, 2880, 1457.1, 1386 (alkyl group), 1743.5, 1239.2 (ester group), 1602.7 (-N=N-group), 1559.3 (-C=C- aromatic stre.), 1164 (ether group), 848.6 (p-sub. benzene ring), 1032 (C-Cl aromatic).

**IR spectrum for n-butyloxy derivative:**  $\nu_{\max}$  /cm<sup>-1</sup> : 3062 (-C-H aromatic stre.), 2958.5, 2875.5, 1458.1, 1390 (alkyl group), 1743.5, 1239.1 (-COO- group), 1603.7 (-N=N-group), 1559.3 (-C=C- aromatic stre.), 1164 (-O- ether group), 849.6 (p-sub. benzene ring), 1030.9 (C-Cl aromatic).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, Standard TMS) for methoxy derivative,  $\delta$ ppm:** 2.45 (s, 3H, Ar-CH<sub>3</sub>), 3.91 (s, 3H, -OCH<sub>3</sub>), 7.04 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.97 (s, 2H, Ar-H), 8.2 (d, 2H, Ar-H).

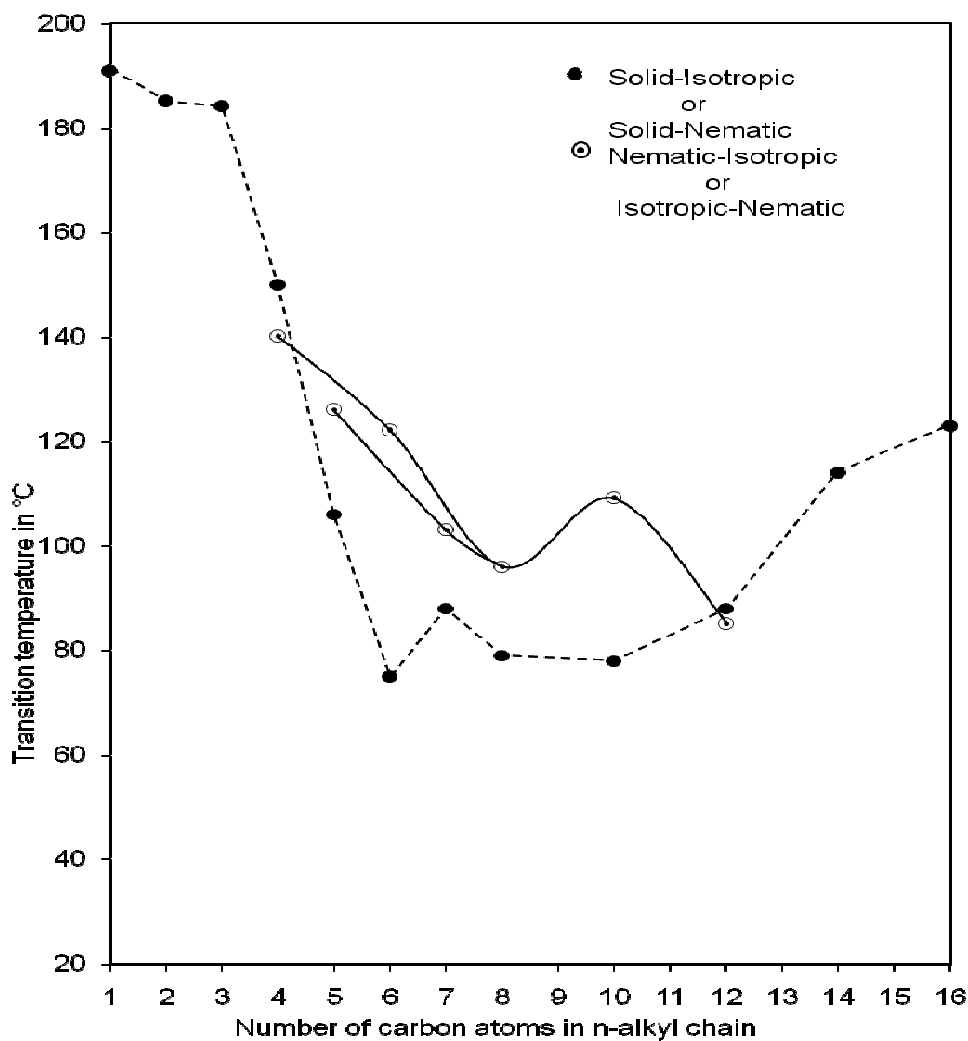
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, Standard TMS) for n-hexyloxy derivative  $\delta$ ppm:** 0.92 (t, 3H, -CH<sub>3</sub>), 1.25-1.48 (m, 6H, 3 X -CH<sub>2</sub>-), 1.83 (m, 2H, -OCH<sub>2</sub>-CH<sub>2</sub>-), 4.06 (t, 2H, -OCH<sub>2</sub>-), 2.45 (s, 3H, Ar-CH<sub>3</sub>), 7.02 (d, 2H, Ar-H), 7.35 (d, 2H, Ar-H), 7.81(d, 2H, Ar-H), 7.97(s, 2H, Ar-H), 8.18(d, 2H, Ar-H),

## RESULTS AND DISCUSSION

4-hydroxy-3,5-dichloro phenylazo-4'-methyl benzene 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''-methyl benzenes are nematogenic in nature. The first three and last two member of the series is non-mesomorphic. Mesomorphism commences from fourth homologue and ends to twelfth homologue. Fifth to tenth homologues are enantiotropic nematic, while fourth and twelfth homologue is monotropic nematic. Thus, totally seven members of the titled homologous series are mesomorphic in nature. Smectic mesophase is totally absent. The transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy group of the homologues. The phase diagram is represented in **figure-1**. The solid-isotropic or solid-nematic transition curve follows a zig-zag path of falling and rising tendency as series is ascended. Solid-isotropic or solid-mesomorphic transition curve steeply falls from first to sixth homologue of the series and then rises for seventh homologue. Then again it leveled off to the eighth homologue and slightly falls to the tenth homologue. Thereafter from tenth homologue, it rises up to the last homologue of the series.

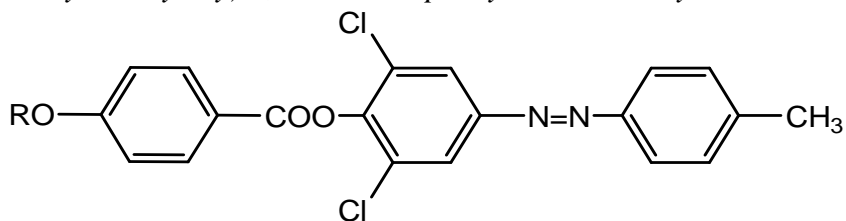
The nematic-isotropic or vice versa transition curve shows falling tendency from fourth to eighth homologue of the series and then tenth homologue of the series shows unusual rise and again falls by 24°C at the last homologue of the series. The usual odd-even effect is observed in nematic-isotropic or isotropic-nematic transition curves with alternation of transition temperatures. Thus, nematic-isotropic (or vice versa) transition curve behaves in normal manner from fourth to eighth homologue and then behaves abnormally due to the presence of polarizable group chloro at the middle phenyl ring. The nematic mesophase appeared has threaded type of texture as judged directly by visualizing the sample of the homologue in a field of view of hot stage polarizing microscope. The nematic-isotropic (or vice versa) transition temperatures are between 88°C and 150°C with mesomorphic range varying from minimum of 15°C at the seventh homologue and maximum of 47°C at the sixth homologue. Thus, the titled homologous series is considered as middle ordered melting type with short range of liquid crystallinity. Liquid crystals of moderate chain lengths yield only nematogenic homologous [9, 10] and is well supported by present investigation.

The non-mesomorphic behaviors of first three and last two members of the homologous series are attributed to the high crystallizing tendency of the respective homologues. Enantiotropic/monotropic nematic property is exhibited by the remaining members of the series due to the statistically parallel orientations of molecules with end to end attraction in floating condition resisting thermal vibrations. Absence of smectic character is attributed to insufficient intermolecular forces of attraction to form sliding layered arrangement of molecule 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 transition curve shows alternation of transition temperatures from fourth to the eighth homologue but alternation diminishes as series is ascended because higher homologues are of even number and in case of higher homologues, the longer left n-alkyl chain of n-alkoxy group may coil or couple 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 other homologous series- A & B [**figure-2**] for their molecular characteristics and thermal stabilities which are shown in **Table-3**.

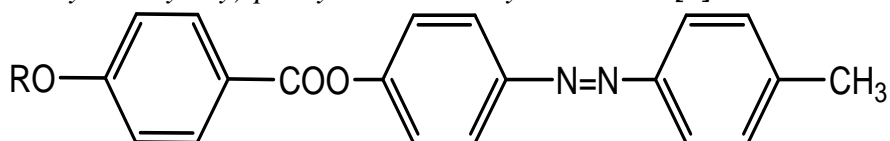


**Figure-1** The phase behaviour of series 1.

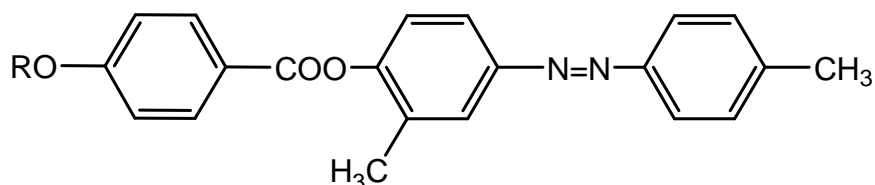
[1] 4-(4'-n-alkoxy benzoyloxy)-3, 5-dichloro phenylazo-4''-methyl benzenes



[A] 4-(4'-n-alkoxy benzoyloxy)-phenylazo-4''-methyl benzenes [8]



[B] 4-(4'-n-alkoxy benzoyloxy)-3-methyl phenylazo-4''-methyl benzenes [11]



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

**Figure-2**

**Table – 3: Average Thermal Stabilities in °C**

Series	Average transition temperatures in °C		
	Series-1 (-3,5-dichloro)	Series-A (-H)	Series-B (-CH <sub>3</sub> )
Smectic-Isotropic Or Smectic-Nematic	-	106.5 (C10-C16)	114.66 (C7-C16)
Commencement of smectic phase	-	C10	C7
Nematic- Isotropic Or Isotropic-nematic	113.42 (C4-C12)	242.0 (C1-C8)	152.14 (C1-C8)
Commencement of nematic phase	C4	C1	C1

The homologous series-1, A & B possess three phenyl rings linked through –COO- and –N=N- central bridges, left n-alkoxy terminal group at para position as well as right methyl end group as common identical moiety, while they differ only by functional groups substituted in the middle phenyl ring. Hence, the variation in mesomorphic characteristics and degree of mesomorphism is varied due to the variation of functional group or groups linked at the middle phenyl ring. The laterally substituted chloro groups at the middle phenyl ring increase intermolecular distance consequently intermolecular forces of attraction may diminish. However, lateral substitution increases the width of the molecule and affects 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 operate at a time. The net effect will depend upon the predominance of two opposing effects. Therefore mesomorphic characteristics of a molecule depend upon the magnitude of the net resultant adhering force of attractions.

Smectic mesophase is totally absent in the case of series-1 because of steric hindrance caused by the 3,5-dichloro group as compared to –H and –CH<sub>3</sub> which keep molecules apart, reducing intermolecular forces of attractions. The average thermal stability of series-A is the highest among the series under comparison because molecules of series-A are long and linear without any substitution at the lateral position. This causes the closest approach of molecules, resulting in the highest magnitude of intermolecular attractions. Thus, it exhibits smectic and nematogenic behavior with the 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 the middle aromatic core, i.e. series-1 has a lateral 3,5-dichloro group attached to the middle phenyl ring, whereas series-A & B have –H and –CH<sub>3</sub> lateral substituents at similar phenyl rings respectively. Thus, as compared to series-A, series-B and series-1 have increased breadth due to the laterally substituted 3,5-dichloro and –CH<sub>3</sub> groups. Gray [9] has explained that an increase in the breadth of the molecules reduces both nematic and smectic mesophase stability. Thus, Gray's view is supported by the present investigation. It seems that the lateral 3,5-dichloro and methyl groups not only increase the breadth of the molecules of series-1 and series-B but also affect considerably

the non co-planarity in the system due to steric interaction. Both these factors would eliminate the smectogenic property for title homologous series-1 under present investigation.

Nematic-isotropic thermal stability of series-1 is lowest as compared to homologous series-A & B, which is because of the increase in molecular breadth and difference in polarity of laterally substituted groups. Thus, from the above discussion the lateral group efficiency order from the nematic-isotropic thermal stability can be derived as under.

Nematic group efficiency order (Lateral substitution):  $-H > -CH_3 > 3, 5\text{-dichloro}$

### CONCLUSIONS

A new homologous series with laterally substituted 3, 5-dichloro group on middle phenyl ring is synthesized. Thermal stability is reduced by lateral substitution and supports the earlier views.

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