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# Study of Azo Ester Mesogens: 4-(4'-n-Alkoxy benzoyloxy)-3-Methoxy- phenyl azo-4"-Nitrobenzenes

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## ABSTRACT

*New mesogenic homologous series having azo-ester central linkages was synthesized. All the homologues of the homologous series exhibit mesomorphism. Mesomorphism commences from the very first members of the series. Smectic mesophase commences from tenth homologue in addition to nematic mesophase. Sixteenth homologue is only smectogenic. The usual odd-even effect is observed in nematic-isotropic transition curve with alternation of transition temperature. Nematic-isotropic and smectic-isotropic (or Sm-N) transition curve behaves in a normal manner. Smectic-isotropic or smectic-nematic transition curve is extrapolated and merged to eighth homologue suggesting absence of smectic mesophase or showing up of only nematic mesophase. Thermal stability and mesomorphic characteristics are compared with other structurally similar known homologous series. Transition temperatures are observed through hot stage polarizing microscope. Analytical data support the structure of molecules.*

**Key words :** Liquid crystal, mesogens, homologues, Nematic, Smectic,

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## INTRODUCTION

Liquid crystals are very special materials in terms of their unique combination of properties. The knowledge of structural property relationships required in the design of new materials to satisfy new advanced applications, like medical field for determination of cancerous area in body to locate the position of magenta while immediate operation of a pregnant women etc, analysis of drugs and chemical using chromatography technique etc. Present work was planned to synthesize new homologous series with varying lateral and terminal substitution and compared with structurally similar previously reported homologous series. Present work is planned to synthesis liquid crystalline material with lower temperature range of liquid crystallinity. Laterally substituted molecular design of a molecule does lower lateral intermolecular forces of attraction due to increased intermolecular separation and hence transition temperatures are relatively lowered as compared to the mesomorphic compounds without lateral substitution and with $-NO_2$ terminally substituted end group.

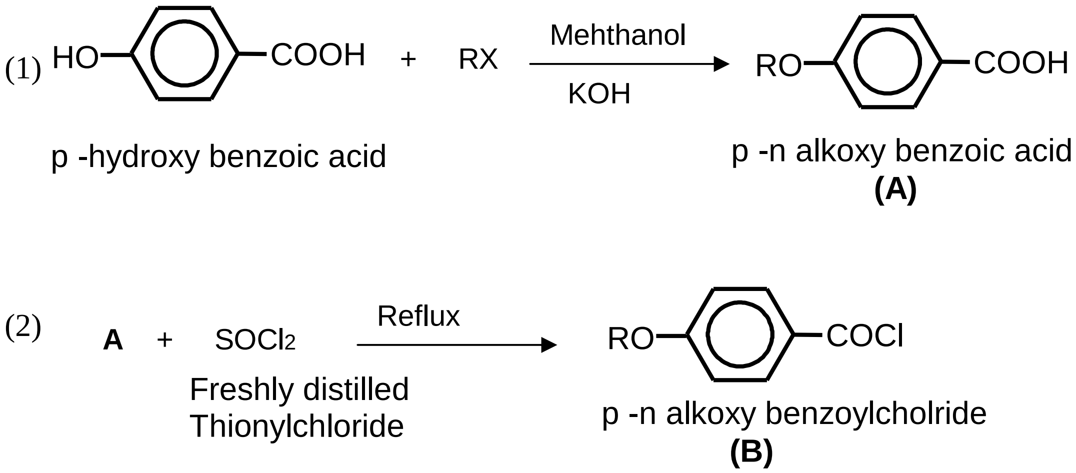
## MATERIALS AND METHODS

### Experimental:

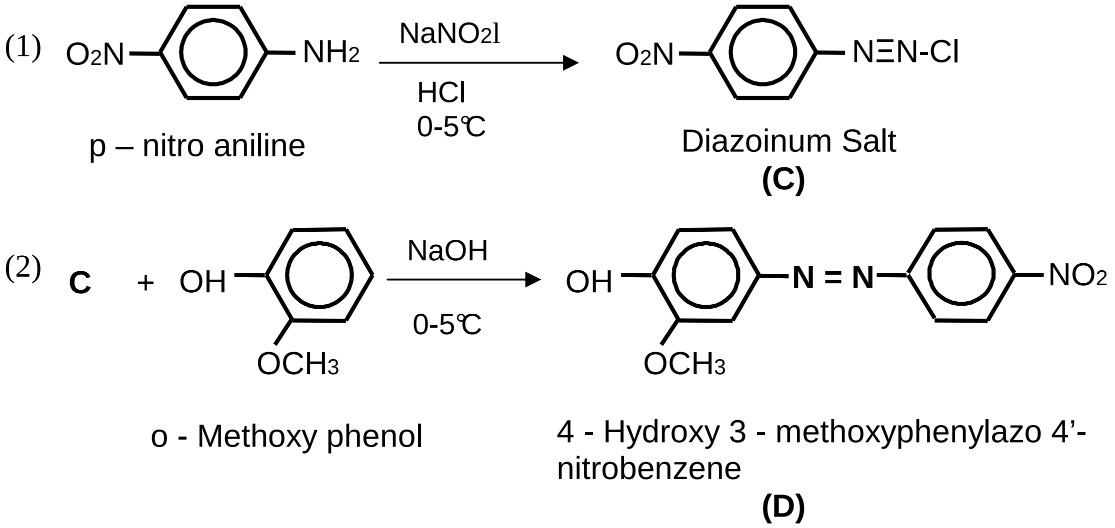
4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenyl azo-4"-nitrobenzenes were prepared by following steps.

(1) p-n alkoxy benzoic acid and from that p-n alkoxy benzoylchlorides were prepared by known method [1].

***Step: 1** Synthesis of p – n alkoxy benzoylchlorides*

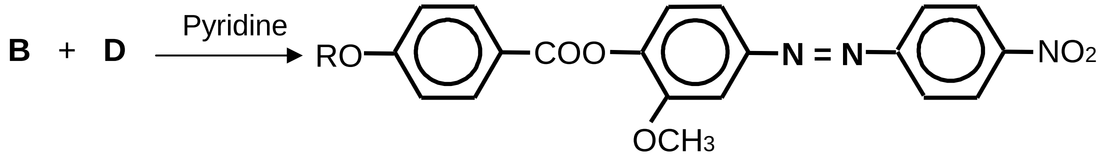


***Step:2** Synthesis of 4- hydroxy 3- methoxyphenylazo 4'- nitrobenzene*



(2) 4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenyl azo-4"-nitrobenzenes were prepared by the method proposed by Vora and Dave [2, 3].

***Step:3** Condensation of compound **B & D***



4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenylazo-4"-nitrobenzenes

The transition temperatures of the homologue of the homologous series were observed through polarizing microscope with heating stage. Analytical data (Table-2) confirms the structure of the homologues.

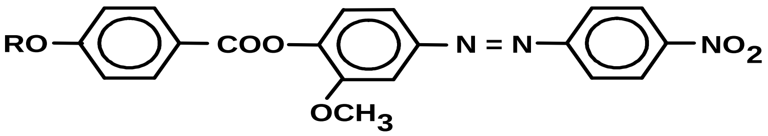
## RESULTS AND DISCUSSION

The transition temperatures of all homologues are reported in table-1. The entire homologous series is mesomorphic in character because mesomorphism is displayed by all the members of the series. Methyl to octyl derivatives of homologues of the series showed only nematic mesophase. Decyloxy to teteradecyloxy derivatives are exhibit polymesomorphic mesophase i.e. nematic and smectic mesophase enantiotropically while last hexadecyloxy homologue is only enantiotropically smectic. The types of smectic mesophase are identified by miscibility method. Decyl, dodecyl and tetradecyl homologues are of the type smectic-A and that of hexadecyl homologue is of type-C. The observed transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal. The phase diagram obtained is represented in figure-I. Smooth curves are drawn through like or related transitions.

The solid-mesomorphic transition curve follows a zig-zag path of rising and overall falling tendency as series is ascended. The nematic-isotropic transition curve shows smooth falling tendency as series is ascended. The usual odd-even effect is observed in nematic-isotropic transition curve with alternation of transition temperature. The smectic-nematic or smectic-isotropic transition curve rises smoothly as series is ascended and merging with the nematic-isotropic transition curve at the sixteenth member of the series. The smectic-nematic or smectic-isotropic transition curve gradually falls in a normal manner from hexadecyl homologue to decyl homologue . It is extrapolated to lower member of the series, so as to determine the latent transition temperature (LTT) for smectic mesophase but it coincides with solid-nematic transition temperature for octyloxy homologue of the series. Thus octyloxy homologue does exhibit only nematic (or absence of smectic) character. The texture of the nematic mesophase is threaded type while that of smectic mesophase is focal conic of the type smectic-A or C determined by miscibility method and by visualizing the sample in a field of view directly hot stage in polarizing microscope.

The above homologous series-(1), (A) & (B) as shown in the **figure-2** have similar linear core structure with three phenyl rings bridged through -COO- and -N=N- group and common left –OR and varying terminal -$NO_2$, -Cl and ***ortho*** -dichloro group. The overall length of the molecule and enhanced lateral group attractions as well as polarizability exhibit on of governs the mesomorphic characteristics and degree of mesomorphism. Therefore the variation in mesomorphic characteristics and degree of mesomorphism are varied because of the variation in terminal end group (-$NO_2$, monochloro and ***ortho*** dichloro) positioned with respect to ***para*** position at central bridge -N=N-. Odd-even effect or alternation of transition temperature is attributed to the presence of odd and even number of methylene units in the left n-alkoxy group for methyl to pentyl homologue. Odd and even methylene units added; affects net intermolecular lateral and terminal forces of attractions which are directly related to the molecular crystal packing [5]. Appearance of mesophases viz. nematic is due to the statistically parallel orientation of molecules causing two dimensional array of molecules by end to end attractions in floating condition and that of smectic is due to lamellar packing causing layered arrangement of molecules in crystal lattices and maintain sliding layered arrangement of molecules on heating the crystal structure of a sample in floating condition under polarized light.

**Table-1 : Transition temperatures of the homologous series : 4-(4'-n-alkoxy benzoyloxy)-3-Methoxyphenylazo-4"-Nitrobenzenes**



| Sr. No. | R = n-alkyl group | Transition temperatures in °C | | |
|---|---|---|---|---|
| | | Smectic | Nematic | Isotropic |
| 1 | Methyl | - | 112.0 | 135.0 |
| 2 | Ethyl | - | 110.0 | 142.0 |
| 3 | Propyl | - | 103.0 | 130.0 |
| 4 | Butyl | - | 104.0 | 129.0 |
| 5 | Pentyl | - | 100.0 | 127.0 |
| 6 | Hexyl | - | 91.0 | 125.0 |
| 7 | Octyl | - | 83.0 | 127.0 |
| 8 | Decyl | 70.0 | 94.0 | 121.0 |
| 9 | Dodecyl | 63.0 | 97.0 | 112.0 |
| 10 | Tetradecyl | 68.0 | 93.0 | 106.0 |
| 11 | Hexadecyl | 71.0 | - | 91.0 |

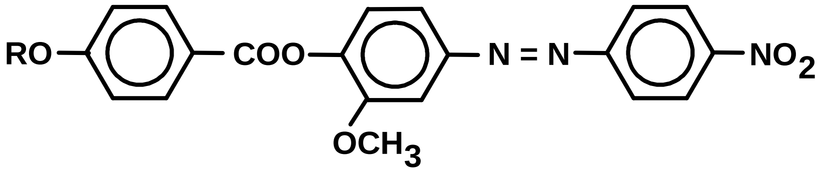
**Table – 2: Elemental Analysis**

| Sr. No. | R = n-alkyl chain | Molecular Formula | Calculated % | Observed % |
|---|---|---|---|---|
| | | | N | N |
| 1. | Methyl | $C_{21}H_{17}N_2O_6$ | 7.12 | 7.20 |
| 2. | Ethyl | $C_{22}H_{19}N_2O_6$ | 6.88 | 6.58 |
| 3. | Propyl | $C_{23}H_{21}N_2O_6$ | 6.65 | 6.42 |
| 4. | Butyl | $C_{24}H_{23}N_2O_6$ | 6.44 | 6.45 |
| 5. | Pentyl | $C_{25}H_{25}N_2O_6$ | 6.24 | 6.30 |
| 6. | Hexyl | $C_{26}H_{27}N_2O_6$ | 6.05 | 5.95 |
| 7. | Octyl | $C_{28}H_{31}N_2O_6$ | 5.70 | 5.18 |
| 8 | Decyl | $C_{30}H_{35}N_2O_6$ | 5.39 | 5.24 |
| 9 | Dodecyl | $C_{32}H_{39}N_2O_6$ | 5.12 | 5.30 |
| 10 | Tetradecyl | $C_{34}H_{43}N_2O_6$ | 4.87 | 4.36 |
| 11 | Hexadecyl | $C_{36}H_{47}N_2O_6$ | 4.64 | 4.57 |

$^1$H NMR 4-(4'-n-decylkoxy benzoyloxy) -3-methoxyphenylazo 4"-nitrobenzenes: (200 MHZ) δ ($CDCl_3$) (ppm) 1.26 ($-CH_3-CH_2$ of $-C_{10}H_{21}$), 3.93 ($-CH_3$ of $-OCH_3$), 4.09 ($-OCH_2$ of $-OC_{10}H_{21}$), 6.898 & 7.338, 8.192 & 8.373 (two p-sub. benzene rings)

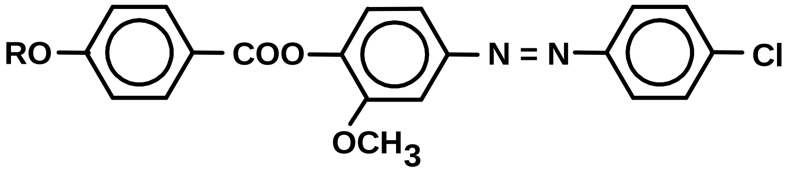
$^1$H NMR 4-(4'-n-Tetradecylkoxy benzoyloxy) -3-methoxyphenylazo 4"-nitrobenzenes: (200 MHZ) δ($CDCl_3$) (ppm) 1.267 (t-$CH_3-CH_2$ of $-C_{14}H_{29}$), 3.929 ($-CH_3$ of $-OCH_3$), 4.054 (,$-OCH_2$ of $-OC_{14}H_{29}$), 6.966 & 7.259, 8.148 & 8.374 (two p-sub. benzene rings), 7.340, 7.697, 8.021 & 7.739 (tri-sub. benzene ring)

**(1)**



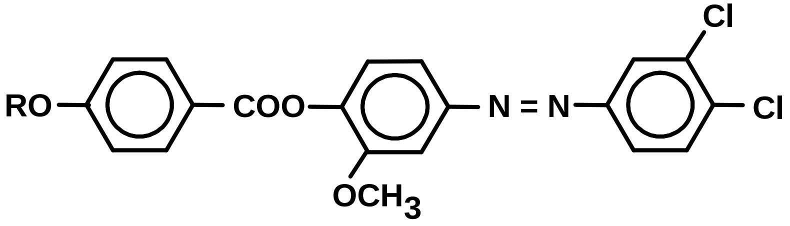
***4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenylazo-4"-nitrobenzenes***

**(A)**



***4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenylazo-4"-chlorobenzenes*** [(4)]

**(B)**



***4-(4'-n-alkoxy benzoyloxy)-3-methoxyphenylazo-3",4"-dichlorobenzenes***[(4)]

**Figure- II**

**Table-3: Average thermal stabilities**

| **Series** → | **Average thermal stabilities in °C** | | |
|---|---|---|---|
| | **(1)** | **(A)** | **(B)** |
| Smectic-isotropic or Smectic-nematic | 93.75<br>($C_{10}$-$C_{16}$) | 87.55<br>($C_4$-$C_{16}$) | 107.5<br>($C_5$-$C_{16}$) |
| Commencement of smectic phase | $C_{10}$ | $C_4$ | $C_5$ |
| Nematic-isotropic or Isotropic-nematic | 124.9<br>($C_1$-$C_{14}$) | 125.6<br>($C_3$-$C_{16}$) | - |
| Commencement of nematic phase | $C_1$ | $C_3$ | - |

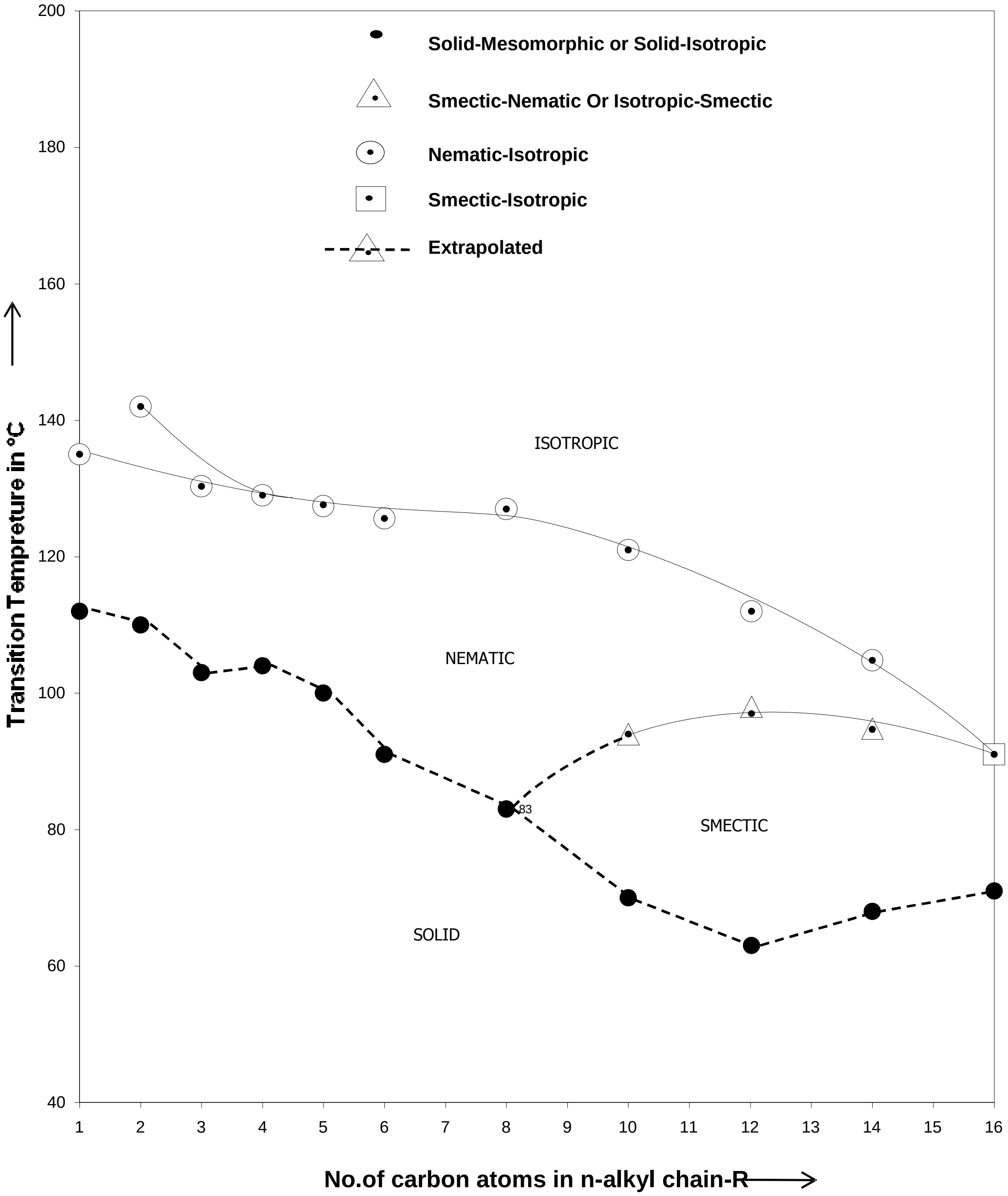


**Figure.I:** **Phase transition diagram for 4-(4'-n-alkoxy benzoyloxy)-3-Methoxyphenylazo- 4''- Nitrobenzenes.**

Though $NO_2$ group is nematogenic but presence of laterally substituted highly polarizable –$OCH_3$ group broadens the molecule and increases width and hence the polarizability of the molecule increases. Thus net intermolecular forces of attractions are balanced out of two opposing effects operating at a time in such way that molecules acquire parallel or/and layered arrangement in floating condition i.e. two dimensional array of molecules is maintained in floating condition on heating the sample which generate nematic or/and smectic mesophase or mesophases for the members of the series. Mesomorphic properties like thermal stabilities of titled homologous series (1) are compared with the structurally similar homologous series (A) and (B) of figure-II.

The relative thermal stabilities of series (1), (A) & (B) are given in **table-3**.

From the table-3 it is seen that smectic thermal stability of series (1) is more than series (A) while it is less than of series (B). This indicates that ***ortho*** dichloro group strengthens the intermolecular forces of attractions as compared to series (1) and (A). However –$NO_2$ functional end group strengthens end to end intermolecular forces of attractions more effectively than monochloro ***para*** substituted group in series (A). Thus intermolecular forces of attractions can be raised by introducing one more chloro group at lateral position of the molecule. Added chloro group surpasses net intermolecular attractive force created by the highly polar group like –$NO_2$ because added substituted chloro group increases polarizability of the molecules of homologous series (B). This results into increase of overall net intermolecular forces of attractions as compared to the homologue to homologue of structurally similar homologous series (1) and (A). Nematic-isotropic thermal stability of series (1) is a little bit less or almost equal to series (A). This suggests that intermolecular forces of attractions operating threaded texture are not much affected by the polarity of the terminal functional group attached to the molecule [6]. This is supported by the ortho dichloro functional group attached to the molecule in series (B) in which nematogenic character is totally absent. In short, smectic thermal stability is affected more by lateral substitution as compared to nematic thermal stability. Exhibition of smectic mesophase is related to extent of non-coplanarity [7,8] caused by the molecule which depend upon the molecular geometry and substituted groups positioned, their size and stereochemistry. In comparison of (1), (A) & (B) extent of non-coplanarity induced by the terminal group –$NO_2$ and –Cl and ***ortho*** dichloro group are different. In comparison of series (1) & (A) the both terminal groups –$NO_2$ and –Cl are positioned at ***para*** are differed in polarity arrangement of atoms in space i.e. stereo arrangement and polarizability. Therefore non-coplanarity induced by –$NO_2$ group is more than –Cl group but at the same time –$NO_2$ group at ***para*** position with respect to –N=N- group stabilize $\pi$-electron more than –Cl group. As a result of this smectic mesophase occurs later i.e. from tenth homologue in series (1);while it occurs from fourth homologue in series (A). In series (B) the third phenyl ring contain one terminal and one lateral group at ***para*** and at ***meta*** position with respect to –N=N- middle group, which shows higher steric hindrance and relatively higher non-coplanarity resulted into occurrence of monotropic smectic mesophase from fifth homologue.

The nematic mesophase commences from very first homologue of the series enantiotropically in case of series (1) while it commences from third homologue in case of series (A). The polarity and the ratio of the polarity to polarizability and length to breadth are responsible for the order of nematic thermal stability and commencement of nematic mesophase

Thus smectic and nematic group efficiency order derived as under, when methoxy group is laterally substituted in molecular geometry

Smectic group efficiency order : *o*-dichloro > -p$NO_2$ > *p*-Cl

In presence of laterally substituted -$OCH_3$ group

Nematic group efficiency order : *p* -Cl ≥ *p*-$NO_2$ > *o*-dichloro

## CONCLUSIONS

A new homologous series of mesogens with –COO- and –N=N- central bridges is synthesized. The order of smectic and nematic group efficiency in presence of laterally substituted methoxy group is as under.

Smectic : *o*-dichloro $> p\text{-NO}_2 > p$-Cl
Nematic : *p* -Cl $\geq p\text{-NO}_2 >$ *o*-dichloro
In presence of laterally substituted $\text{-OCH}_3$ group

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