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**Der Pharma Chemica, 2010, 2(4): 30-37**
*(http://derpharmachemica.com/archive.html)*

**ISSN 0975-413X**

# Synthesis, characterization and mesomorphic properties of azoester mesogens: 4-n-alkoxy benzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester

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## Abstract

*A new homologous series of azomesogens, 4-n-alkoxy benzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester is synthesized. Mesomorphism commences from the very first homologues of the series and continues up to tetradecyl derivatives. Last hexadecyl derivative is non-mesomorphic. All mesomorphic homologues are enantiotropic nematic. Thus, present homologues series is purely nematogenic. The usual odd-even effect is observed in nematic-isotropic transition curve. Transition curve behaves in a normal manner. The average thermal stability and mesomorphic characteristics are compared with structurally similar homologues series. Series is of middle ordered melting type without display of smectic character even in the last member of the series.*

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## INTRODUCTION

Thermo-tropic liquid crystals are of great technological importance [1]. Terminal and lateral substituents and geometrical shape of a molecule play an important role in mesomorphic properties of a mesogen. Generally, the terminal substituent's comprise of either a homologue alkoxy or alkyl groups or a compact unit such as nitro, cyano, halogen, etc. [2, 3]. A number of mesogenic homologues series of achiral esters with branched alkyl tail are also reported in the literature [4, 5]. A number of homologues series which have different molecular structures were synthesized by researchers earlier in order to establish the correlation between chemical constitution and Mesomorphism [6-10]. Presently, we have synthesized a new homologues series comprising of –N=N- and –COO- central linkages.

## MATERIALS AND METHODS

All the chemicals used were of laboratory grade. *P*-n-alkoxy benzoic acid and *P*-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave *et al.* [11]

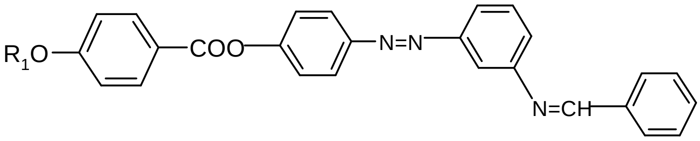
***1)Preparation of p-n-alkoxy benzoic acids***

p-Hydroxy benzoic acid (0.1 mole) corresponding alkyl halides (0.12 mole) and KOH (0.25 mole) were dissolved in 100 ml methanol and reaction mixture was refluxed for 3 to 4 hr. 10% aqueous KOH solution (20 ml) was added and refluxing continued for further two hours to hydrolysis any ester formed. The solution was cooled and acidified with HCL to precipitate. The corresponding alkoxy acids for the higher members the total refluxing period was extended to 7 to 8 hours. The alkoxy acids were crystallized from ethanol or acetic acid till them melting points and transition temperatures.

***2) Preparation of p-N alkoxy benzoyl chlorides***

*p*-n alkoxy benzyl chlorides were prepared by heating the corresponding p-n alkoxy benzoic acids with freshly distilled thionyl chloride in water bath till evolution of hydrogen gas cased. Excess of thionyl chloride was distilled off under reduce pressure using water pump. The acid chlorides left behind were directly used for further reaction without purification.

**3)** 4-(3-amino-phenylazo)-phenol was prepared by known procedure [12]. The azodye filtered, washed with water, dried and crystallized in glacial acetic acid several time till constant m.p obtained m.p. 148.0°c. The yield is about 69.6%.



Where,

$R_1$ = $(CH_2)_{1\ \text{to}\ 12}$

**Table 1: Transition temperature for 4-n-alkoxy benzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester**

| *Sr. No* | *N-Alkyl group* | *Transition temp (°c)* | | |
|---|---|---|---|---|
| | | *K-S Smetic* | *S-N Nematic* | *N-T Isotropic* |
| 1 | Methyl | - | - | 185.0 |
| 2 | Ethyl | - | - | 193.0 |
| 3 | Propyl | - | 146.0 | 151.0 |
| 4 | Butyl | - | 144.0 | 161.0 |
| 5 | Pentyl | - | 121.0 | 152.0 |
| 6 | Hexyl | - | 106.0 | 154.0 |
| 7 | Heptyl | 95.0 | 98.5 | 143.0 |
| 8 | Octyl | 100.0 | 109.0 | 147.0 |
| 9 | Decyl | 95.3 | 120.0 | 142.5 |
| 10 | Dodecyl | 96.0 | 131.5 | 139.0 |
| 11 | Tetrudecyl | 92.0 | 130.5 | 135.0 |
| 12 | Hexadecyl | 85.0 | - | 132.0 |

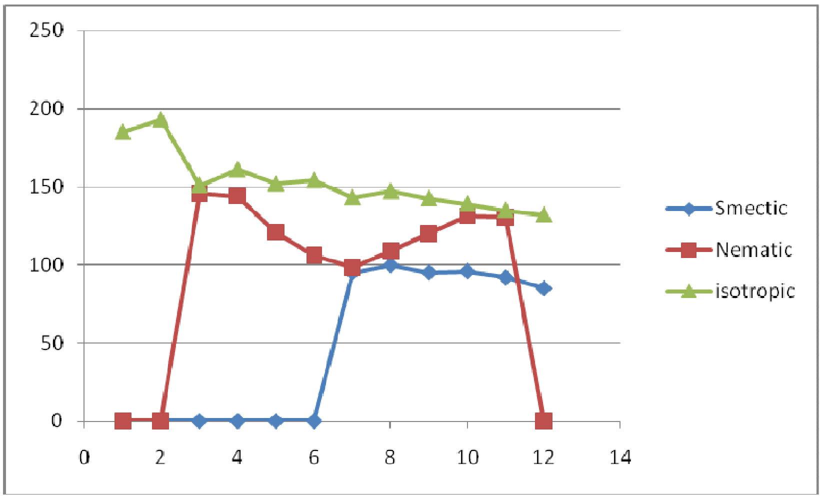
**4)** Preparation of 4-Hydroxy –benzoic acid 4-(3-amino-phenylazo)-phenyl were synthesized by adding drop-wise a solution of 4-(3-amino-phenylazo)-phenol in pyridine to an ice cooled solution of respective 4-alkoxy benzoyl chloride with constant stirring. The reaction mixture was warmed for half an hours and allowed to stand overnight at room temperature. It was acidified with 1:1 cold HCL and finally pure product were obtained by subsequent usual steps. The resulting products were obtained were purified by silica gel column chromatography using petroleum ether (60-80°c) and ethyl acetate mixture (95:5) as eluent and crystallized by alcohol and benzene (80:20) until constant transition temperatures obtained and recorded in Table 1. Then it was reacted with benzaldehyde to afford Schiff bases no.1 to 12 (Table 1). Liquid crystalline properties were investigation on a leitz labourlux polarizing microscope with a heating stage. Analytical data supports the structure [Table 2, 3(a) and 3(b)]

## RESULTS AND DISCUSSION

4-(3-amino-phenylazo)-phenol is a non-liquid crystal substance but linking of phenyl ring bridge through –COO- and left n-alkoxy terminal induces mesomorphic character. Homologous series, 4-Hydroxy –benzoic acid 4-(3-amino-phenylazo)-phenyl is entirely enatiotropic nematogenic except hexadecyl derivative, which is nonmesogenic. Smetic mesophase is totally absent for any members of the series.

The transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of the left n-alkoxy groups from Table 1. Curves are drawn through the related points as shown in Fig. 1. The solid-nematic or solid-isotropic transition curve follows a zigzag path of rising and falling as series is ascended. Zigzag path of solid-nematic and nematic-isotropic transition curve is due to the sequential addition of –$CH_2$- methylene unit at the left n-alkoxy group. This causes difference in the length and linearity of the molecule 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 member 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 even member of the series. The nematic isotropic transition curve for odd and even member of the series initially rise and thereafter falls up to the fourteenth homologue of the series in usual manner. First and second members of the series do not melt sharply at definite temperature bur decompose at higher temperatures. Usual odd-even effect is observed in nematic-isotropic transition curve. The texture of the nematic mesophase is threaded type as judged directly by observing the sample in a field of view of polarizing microscope.

**Fig.1: Transition temperatures Vs Number of carbon atoms**



Thus, the present homologues series under discussion can be considered as middle ordered melting type with mesophase length minimum of 38.0°c at the twelfth member and maximum of 161.0°c at the second member of the series.

**Table 2: Elemental analysis for 4-n-alkoxy benzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester**

| ***Sr. No*** | ***N-Alkyl group*** | ***Molecular Formula*** | ***%Nitrogen*** | |
|---|---|---|---|---|
| | | | ***Calcd.*** | ***Obs.*** |
| 1 | Methyl | $C_{27}H_{21}N_3O_3$ | 9.65 | 9.60 |
| 2 | Ethyl | $C_{28}H_{23}N_3O_3$ | 9.35 | 9.30 |
| 3 | Propyl | $C_{29}H_{25}N_3O_3$ | 9.07 | 9.00 |
| 4 | Butyl | $C_{30}H_{27}N_3O_3$ | 8.80 | 8.80 |
| 5 | Pentyl | $C_{31}H_{29}N_3O_3$ | 8.55 | 8.50 |
| 6 | Hexyl | $C_{32}H_{31}N_3O_3$ | 8.31 | 8.30 |
| 7 | Heptyl | $C_{33}H_{33}N_3O_3$ | 8.09 | 8.00 |
| 8 | Octyl | $C_{34}H_{35}N_3O_3$ | 7.87 | 7.80 |
| 9 | Decyl | $C_{35}H_{37}N_3O_3$ | 7.67 | 7.66 |
| 10 | Dodecyl | $C_{36}H_{39}N_3O_3$ | 7.48 | 7.41 |
| 11 | Tetrudecyl | $C_{37}H_{41}N_3O_3$ | 7.30 | 7.30 |
| 12 | Hexadecyl | $C_{38}H_{43}N_3O_3$ | 7.12 | 7.10 |

Enatiotropic nematic property is shown from very first member of the series except last member of the series, due to the parallel orientations of molecules with end to end attractions in floating condition resisting thermal vibrations. Last member of the homologues series is nonmesogenic because of its high crystallizing tendency and the incapability of intermolecular cohesion forces to maintain parallel orientation in the floating condition or to form layered arrangement of molecules. Smectic mesophase is totally absent for all members of the present homologues series-1 because of the extent of non co planarity caused by the molecules and resulted intermolecular force of attractions are incapable to maintain layered arrangement of the molecules even in the momotropic condition. It is seen that nematic-isotropic transition curve shows alternation of transition temperature from third to the eighth homologues but alternation diminishes as series is ascended because higher homologues, the longer left n-alkyl chain of n-alkoxy group may be coiled 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 homologues.

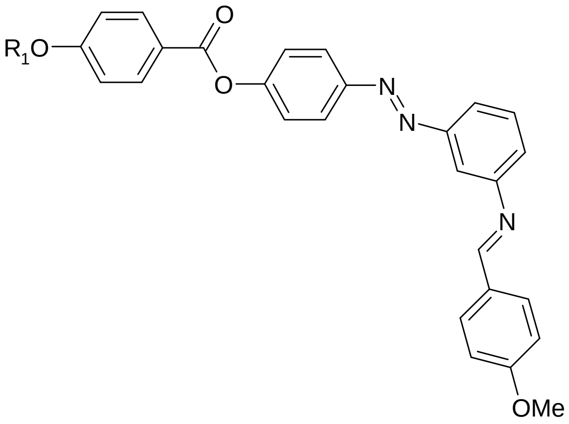
**Table 3(a). Spectral data**

| Homologue | IR Spectral ($cm^{-1}$) |
|---|---|
| Methyl | 2934.0, 2846.0, 1462.0, 1375.2 $cm^{-1}$ → Alkyl group |
| | 1727.1, 1252.7 $cm^{-1}$ → -COO- (Ester group) |
| | 1595.0 $cm^{-1}$ → -N=N- (Azo group ) |
| | 1559.3 $cm^{-1}$ → -C=C- (Aromatic str.) |
| | 1142.7 and 1167.8 $cm^{-1}$ → -O- (Ether group ) |
| | 839.9 $cm^{-1}$ → *P*-sub. Benzene ring |
| | 763.8 $cm^{-1}$ → tri sub. Benzene ring |
| | IR confirms above structure |
| n-Dodecyl | 2919.0, 2848.7, 1457.1, 1338.0 $cm^{-1}$ → Alkyl group |
| | 1744.0, 1258.5 $cm^{-1}$ → -COO- (Ester group) |
| | 1602.0 $cm^{-1}$ → -N=N- (Azo group ) |
| | 1559.3 $cm^{-1}$ → -C=C- (Aromatic str.) |

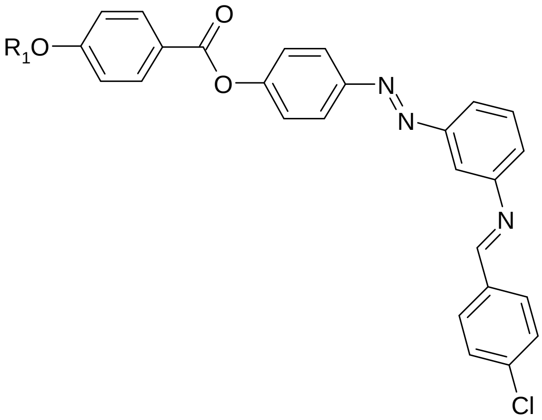
| | |
|---|---|
| | 1144.7 and 1169.7 cm$^{-1}$ → -O- (Ether group ) |
| | 845.7 cm$^{-1}$ → *P*-sub. Benzene ring |
| | 771.5 cm$^{-1}$ → tri sub. Benzene ring |
| | IR confirms above structure |
| | |

**Table 3(b). Spectral data**

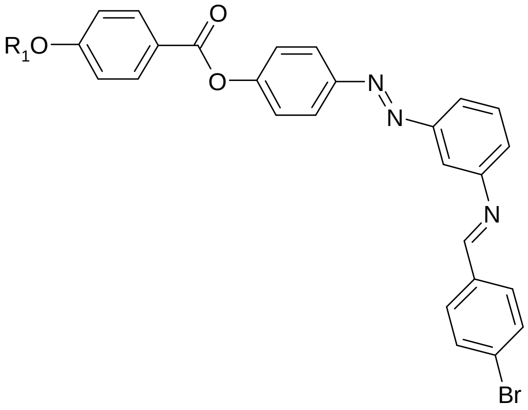
| Homologue | NMR Spectra δ (ppm) |
|---|---|
| n-butyl | 0.98 (3H, t, -CH$_3$) |
| | 1.50 (2H, m, -CH$_2$-) |
| | 1.82 (2H, t, -OCH$_2$-CH$_2$-) |
| | 4.06 (2H, t, OCH$_2$-) |
| | 2.73 (3H, s, -phCH$_3$) |
| | 3.90 (3H, s, -OCH$_3$) |
| | 6.90-8.17 (11H, m, Ar-H) |
| n-pentyl | 0.95 (3H, t, -CH$_3$) |
| | 1.41-1.46 (4H, m,2 X -CH$_2$-) |
| | 1.81 (2H, t, -OCH$_2$-CH$_2$-) |
| | 4.02 (2H, t, OCH$_2$-) |
| | 2.73 (3H, s, -phCH$_3$) |
| | 3.89 (3H, s, -OCH$_3$) |
| | 6.90-8.17 (11H, m, Ar-H) |



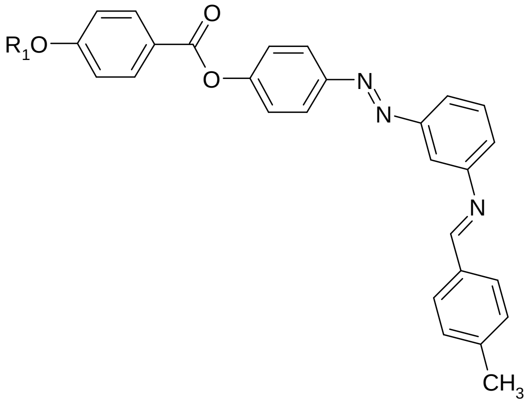
(1) 4-alkoxy-benzoic acid 4-{3-[(4-methoxy-benzylidene)-amino]-phenylazo}-phenyl ester



(A) 4-alkoxy-benzoic acid 4-{3-[(4-chloro-benzylidene)-amino]-phenylazo}- phenyl ester



(B) 4-alkoxy-benzoic acid 4-{3-[(4-bromo-benzylidene)-amino]-phenylazo}- phenyl ester



(C) 4-alkoxy-benzoic acid 4-{3-[(4-methyl-benzylidene)-amino]-phenylazo}- phenyl ester

**Fig.2**

The mesomorphic characteristics of the title homologues series-I are compared with geometrically identical homologous series-A, B and C (Fig. 2). The homologues series-I, A, B and C posses fourth phenyl rings, linked through -COO-and –N=N- central bridges, left n-alkoxy terminal group at the *para* position to –N=N- unit at middle phenyl ring as common identical features, while they differ only by right functional terminal groups substituted at third phenyl ring. Therefore, mesogenic behavior and degree of Mesomorphism of the series under comparison is varied due to the variation of functional group and group linked at the fourth phenyl ring only. These functional group are –$OCH_3$, -Cl, -Br and -$CH_3$ for series –I A, B and C respectively. They differ in size, polarity, polarizability and affecting planarity of molecule as well as creation of steric hindrance in addition to other factors, responsible for intermolecular forces of cohesion. Thus variation of intermolecular forces cohesion and end to end attractions are directly related to mesomorphic behavior and degree of Mesomorphism. The average thermal stabilities of series-I, A, B and C are given in Table 4. Nematic-isotropic average thermal stability of homologues series-I is the highest amongst the group of homologues series-I , A, B and C (Table 4). Relatively the highest polarity and polarizability of terminally attached –$OCH_3$ functional group with respect to –Cl, -Br and –$CH_3$ raised the intermolecular forces of attractions and hence resulting into highest nematic-isotropic thermal stability. Late commencement of occurrence of nematic mesophase in case of series-B and C i.e the series with –Br and –$CH_3$ terminals may be due to their bigger size steric hindrance and lower polarity affecting end to end intermolecular forces of attractions; incapable of maintaining parallel orientations of molecules in floating condition increasing crystallizing tendency of early homologues. Extent of co planarity caused by molecules of series-I is not enough to maintain layered arrangement of the molecules and hence smectic mesophase does not occur even up to the last homologue. Therefore relative average thermal stability for the smectic does not require to be discussed. The study suggest the following terminal group efficiency order for nematic, on the basis of thermal stability as under,

$$-OCH_3 > -Cl > -Br > -CH_3$$

**Table 4 Average thermal stabilities**

| | **Average transition temp. (°C)** | | | |
|---|---|---|---|---|
| Series | Series-(1) | Series-(A) | Series-(B) | Series-(C) |
| | ($-OCH_3$) | ($-Cl$) | ($-Br$) | ($-CH_3$) |
| Nematic-isotropic or Isotropic-nematic | 162.18<br>($C_1$-$C_{14}$) | 142.0<br>($C_1$-$C_{16}$) | 139.0<br>($C_4$-$C_{16}$) | 103.9<br>($C_3$-$C_{16}$) |
| Commencement of Nematic phase | $C_1$ | $C_1$ | $C_4$ | $C_3$ |

## CONCLUSION

The synthesis of new mesogenic homologues series of azoester derivatives is carried out. All the members of the series exhibit enatiotropic nematic Mesomorphism with absence of smectic property. The average thermal stability of present homologues series-I is higher than those of structurally related compounds, which can be attributed to the high polarity and polarizability of the molecule due to $-OCH_3$ terminal.

**Acknowledgement**
The authors are thankful to M.V.M. Science College , Rajkot ,The Nadiad Education Society, Nadiad and the principal Dr. K. J. Ganatra and the principal Dr.A.M.Patel and HOD D.M. Patel for the necessary facilities.

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