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SYNTHESIS OF 4-(3-((4-HYDROXYBENZYL)OXY)3-OXOPROP-1-EN-1-YL)PHENYL-4-N- ALKOXY BENZOATE

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ABSTRACT

The titled homologous series consists of 11 members. The methyl to pentyl homologues are nonmesomorphic because of very high melting points, however, the hexyl to hexadecyl derivatives are enantiotropic nematic with absence of smectogenic. The texture of nematic mesophase is threaded or Schlieren. The nematic-isotropic transition curve of the phase diagram behaves in a normal manner. The transition temperatures of the series and liquid crystal properties are observed through optical polarizing microscopy and a hot stage. The novel materials were characterized by elemental analysis, infrared, and 1H NMR spectroscopy. Analytical data support the molecular structures. The liquid crystal properties of the novel series are compared with structurally similar homologous series. The novel series is entirely nematogenic with absence of smectic character and of a middle-ordered melting type. The nematic-isotropic thermal stability varies between around 140^{0}C and 175^{0}C.

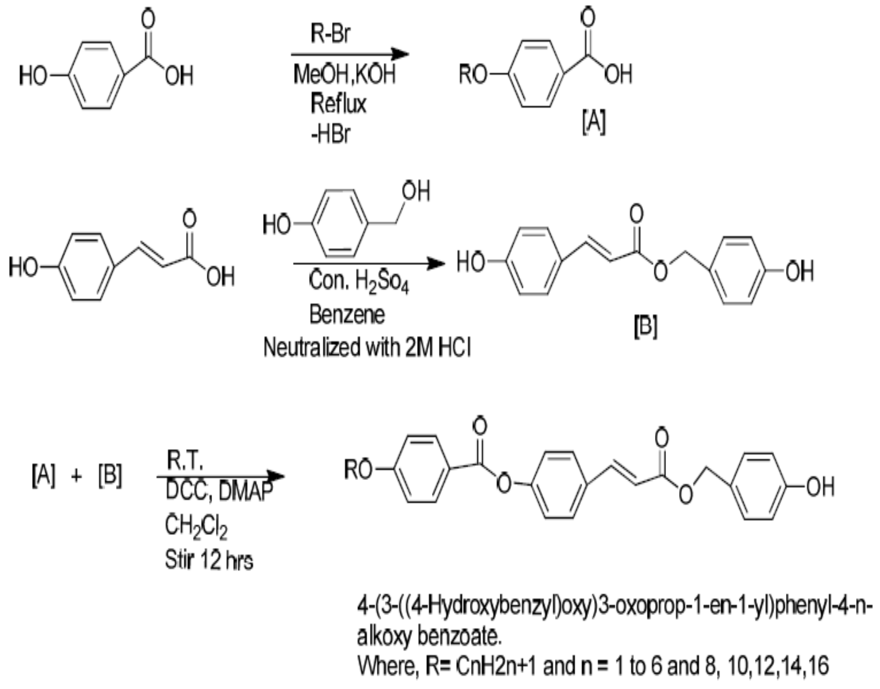
KEYWORDS: Anisotropic; liquid crystal; mesomorphic; nematic; smectic.

INTRODUCTION

The basic prime requirement to induce liquid crystalline properties in a substance is a suitable compromise of molecular rigidity and flexibility.[1–3] Molecular rigidity and flexibility occurs as a consequence of the molecular shape, size, and aromaticity types of the central, terminal, and lateral groups, and their polarities, molecular polarity, and polarizability, etc. Thus keeping these issues in view to synthesize novel liquid crystals (LC) substances, the molecular structure of the novel series was designed with three phenyl rings bridged through −COO− and−CH=CH−CO− central groups, and −OR, −OH as left and right terminal groups, respectively, without any lateral groups. The aim of the present work is to further establish the relationship between liquid crystal properties and molecular structure.[4]

Experimental

4-Hydroxybenzoic acid was alkylated by a suitable alkylating agent (A) and Component (B) is prepared by reacting p-Hydroxy cinnamic acid with corresponding freshly distilled p-Hydroxy phenyl ethanol in presence of concentrated sulphuric acid mixture. p-n- alkoxy benzoic acids dissolved in MDC with component (B) is in portions with DCC & DMAP as catalyst by stirring reaction mixture.[5] Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy cinnamic acid, alkyl halides (R-X), p-Hydroxy phenyl ethanol, KOH, DCC, DMAP, MDC etc. required for synthesis were used as received except solvents which were dried and is tilled prior to use. The synthetic route to the series is mentioned below in **Scheme** obtained.



Reaction Scheme.

Table 1: Physical constants.

Series-4				
Compound	***R (n-alkyl chain)***	***M. F.***	***M. Wt.***	***Yield (%)***
1	Methyl	$C_{24}H_{20}O_6$	404	60
2	Ethyl	$C_{25}H_{22}O_6$	418	82
3	Propyl	$C_{26}H_{24}O_6$	432	86
4	Butyl	$C_{27}H_{26}O_6$	446	68
5	Pentyl	$C_{28}H_{28}O_6$	460	72
6	Hexyl	$C_{29}H_{30}O_6$	474	82
7	Octyl	$C_{31}H_{34}O6$	502	66
8	Decyl	$C_{33}H_{38}O6$	530	85
9	Dodecyl	$C_{35}H_{42}O6$	558	73
10	Tetradecyl	$C_{37}H_{46}O6$	586	80
11	Hexadecyl	$C_{39}H_{50}O6$	614	77

Elemental analysis

Compound	***M. F.***	**Elements % Found**			**Elements % Calculated**		
		C	**H**	**O**	**C**	**H**	**O**
Propyl	$C_{26}H_{23}NO_7$	72.21	5.59	22.20	72.20	5.50	22.25
Butyl	$C_{27}H_{25}NO_7$	72.63	5.87	21.50	72.68	5.80	21.56
Pentyl	$C_{28}H_{27}NO_7$	73.03	6.13	20.84	73.75	6.10	20.82

- **Spectral Data**

IR (KBr) in cm^{-1} for butyloxy derivative (C-8)

806 & 891 cm^{-1} pera di substituted phenyl ring 1031, 1087, 242 cm^{-1} ether linkage, 1448,1625 cm^{-1} aromatic ring, 1568, 1309 nitro group present,1708 cm^{-1} ester present, 2850, 2927 long chain alkane present, 3323 –OH Phenolic Present.

IR (KBr) in cm^{-1} for hexayloxy derivative(C-12)

767 & 891 cm^{-1} pera di substituted phenyl ring 1031, 1087, 1255 cm^{-1} ether linkage, 1450,1627 cm^{-1} aromatic ring, 1566,1309 nitro group present,1703 cm^{-1} ester present, 2850, 2927 long chain alkane present, 3323 –OH Phenolic Present.

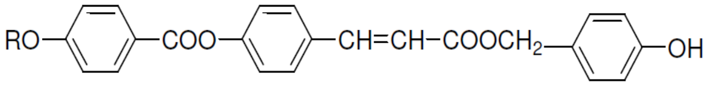
^{1}*H* NMR (CDCl$_3$) in ppm for Decyloxy derivatives (C-02).

0.83-0.98 (t, 3H,-CH_3 of –OC_2H_5 group), 2.03(Q, 2H, Ar-O **-CH_2**), 4.45(S, 2H, Ar-CH_2 –COO), 6.14 (d, 1H of –CH=C**H**), 6.89(d, 2H, Ar-H), 6.97 (d, 2H, Ar-H),6.99 (d, 1H, -C**H**=CH), 7.26 (d, 2H, Ar-H), 7.37(d, 2H, Ar-H), 7.67 (d, 2H, Ar-H), 8.27(d, 2H, Ar-H). 8.32 (S, 1H, -OH).

^{1}H NMR ($CDCl_3$) in ppm for Tetradecyloxy derivatives (C-06)

0.83-0.98 (t, 3H,-CH_3 of –OC_6H_{13} group), 1.00-1.10 (m, 6H, polymethylene group of –OC_6H_{13}), 1.39-1.53(m, 2H, Ar-O-(CH_2)-**CH_2**), 1.92-2.28(p, 2H, Ar-O-CH_2 of–OC_6H_{13}), 3.61(S, 2H, Ar-CH_2 – COO), 4.60 (d, 1H of –CH=C**H**), 6.79(d, 2H, Ar-H), 6.89 (d, 2H, Ar-H),6.02 (d, 1H, -C**H**=CH), 7.10 (d, 2H, Ar-H), 7.31(d, 2H, Ar-H), 7.44 (d, 2H, Ar-H), 8.81(d, 2H, Ar-H). 8.90 (S, 1H, -OH).

Table 2: Transition temperatures of 4-(3-((4-Hydroxybenzyl)oxy)3-oxoprop-1-en-1-yl)phenyl-4-n-alkoxy benzoate Derivatives.



Sr. No.	n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	169
2	Ethyl	-	-	180
3	Propyl	-	-	174
4	Butyl	-	-	168
5	Pentyl	-	-	179
6	Hexyl	-	139	152
7	Octyl	-	141	155
8	Decyl	-	145	160
9	Dodecyl	-	152	166
10	Tetradecyl	-	158	174
11	Hexadecyl	-	155	162

4-*n*-Alkoxy benzoic acids are dimeric. Their dimerization disappears by esterification due to the breaking of hydrogen bonding. The novel mesogenic series consists of 11 homologues. The methyl to Pentyl homologues are not liquid crystalline, however, all the other homologues from hexyl to hexadecyl are enantiotropically nematogenic without the exhibition of smectogenic character. The transition temperatures **(Table 2)** were plotted versus the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal chain.

The phase diagram shows the phase behavior of the series **(Fig. 1).** The solid-isotropic or nematic transition curve rises and falls in a zigzag manner as the series is ascended with an overall descending tendency. The nematic-isotropic transition curve rises and then gradually falls as the series is ascended and overall behaves in a normal manner. The odd–even effect does not observed. The nematogenic phase temperature range varies between 7◦C and 16◦C.

The isotropic temperatures of LC homologues vary between 152◦C and 174◦C. The methyl to Pentyl derivatives of the series are not mesomorphic because of their high crystallizing tendency, which arises from their strong intermolecular attractions due to presence of shorter methyl to Pentyl *n*- alkyl chains, but the lack of anisotropic intermolecular forces of attraction precludes mesomorphism. As the *n*-alkyl chain length increases, the crystalline character gradually diminishes and the amorphous character of a resultant product increases. The molecules of methyl and ethyl homologues initially attempt to resist the exposed thermal vibrations strongly, but then suddenly lose their ability to withstand the heat. Therefore, finally they sharply and smoothly transform into the isotropic state. The exhibition of the nematogenic mesophase from the propyl to hexadecyl homologues is attributed to the disalignment of molecules at an angle of less than 90◦ with the plane of a surface due to the occurrence of suitable magnitudes of anisotropic intermolecular forces of attraction as a consequence of favorable molecular rigidity and flexibility in floating condition.[1–4] Thus, the molecules arrange themselves in a statistically parallel orientational order at a particular temperature t_1 and continue to float in the same manner up to a higher temperature t_2 with two-dimensional order of the molecules. From and beyond t_2 temperature the molecules are randomly oriented in all possible direction, which is the isotropic liquid state. The nematic mesophase formation takes place in a reversible manner from t_1 and t_2 and on cooling the melt. The temperature difference t_2 and t_1 is called nematogenic phase temperature range, which varies from 7◦C and 16◦C in the novel series. The absence of smectogenic character is attributed to the absence of lamellar packing of molecules in their crystal lattices, and a sliding layered arrangement of molecule does not occur in floating condition. The occurrence of an odd–even effect and the variation of mesomorphic properties from homologue to homologue for the same series is attributed to the sequentially added methylene unit[4] at the *n*-alkyl chain of left *n*-alkoxy terminal chain. The maximum mesomorphic (nematic) phase temperature range is 16◦C at the tetra decyl homologue and the minimum phase length is 7◦C at the hexadecyl homologue. The smooth descending tendency of N-I transition curve is attributed to the gradual variation of molecular rigidity in combination with flexibility[1–3] caused by the progressively and sequentially added methylene unit. The present series is entirely nematogenic with middle-ordered melting type. The statement that “a homologous series with nitro group as substituent is nematogenic” is very well supported by the present investigation and it supports earlier research.[4,9]

The mesogenic behaviour of present series-1 are compared with structurally similar homologous series **X**[10] as shown in **figure-2**. Novel homologous series-**1** and **X** are identical with respect to three phenyl rings and central bridge linking first and middle phenyl ring.

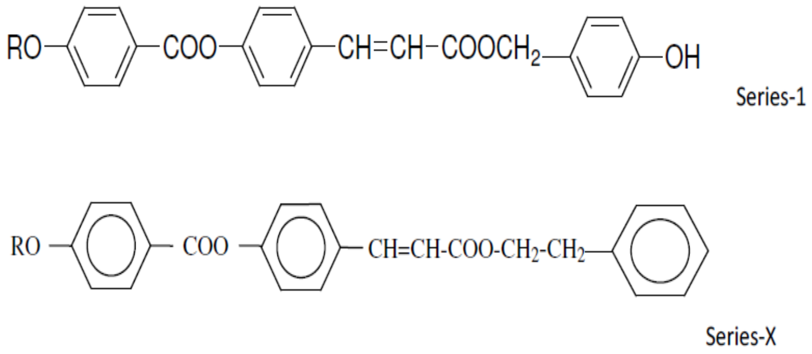


Figure-2.

Moreover left n-alkoxy flexible terminal end group CnH2n+1 i.e. RO- are the same for the same homologue from series to series. But remaining part of each series differs with each other. i.e. series-1 and X differs with respect to terminal end group linking and third phenyl rings as and i.e. molecular rigidity differs but molecular flexibility remains unaltered. Homologous series-1 and series X are identical with respect to central bridge linking middle and third phenyl rings as differs with respect to –$CH=CH-COO-CH_2-Ph-OH$(p) and -$CH=CH-COO-CH_2-CH_2-Ph$ respectively for the same homologue from series to series i.e. molecular flexibility is altered keeping molecular rigidity unaltered for the same homologue from series to series. Thus, variations in mesogenic properties and the degree of mesomorphism observed, are depended upon the altering magnitudes of either molecular rigidity or the molecular flexibility among the presently investigated series-1 and the homologous series – X chosen for comparative study. Following tabl-3 represents some mesogenic properties like average thermal stabilities, commencement of mesophase or mesophases, mesophase lengths etc. to indicate effect of molecular structure on liquid crystal properties in terms of or as a consequence of altering molecular rigidity or flexibility; as under.

Table 3: Average thermal stability in °C.

Series	**1**	**X**
Nematic-Isotropic commencement of nematic phase	161.5˚ (C_6 - C_{16}) C_6	167.6 ˚C. (C_3-C_{16}) C_3
Mesophase length range in °C from (Sm+N)	7◦C - 16◦C C_{16} C_{14}	8 - 37˚C C_{16} C_6

From above table-3, it is clear that,

- Presently investigated novel series -1 and X are only nematogenic.
- Nematic mesophase commences from C_6 homologue of series-1 whereas it commences from C_3 homologue of the series X respectively.
- Total Mesophase length range of series-1 is relatively lower than series- X .

Mesogenic characteristics difference of a substance varies with changing structural part of a molecules under comparison. The changing molecular structural part between series-1 and X is a terminal end group to –CH=CH-COO-CH_2-Ph-OH(p) and -CH=CH-COO-CH_2-CH_2-Ph. Both central bridges contributes molecular rigidity of different magnitude though -CH=CH- unit as commonly present in Series 1 and X. The remaining uncommon part, other than -CH=CH common unit are -CH_2-Ph-OH(p) for series -1 and –CH_2-CH_2-Ph for series –X respectively. The-CH_2-Ph-OH(p) unit of series-1 is longer than –CH_2-CH_2-Ph group of series –X which links with– Ph ring common unit of all series under comparison. Thus, longer and shorter differing units of present novel series-1 and X bonded with differ tail unit -CH_2-Ph-OH(p) and –CH_2-CH_2-Ph through sp_3 or sp_2 carbon respectively. Such differences induces differences into molecular polarity and polarizability as a consequence of molecular rigidity, keeping molecular flexibility unchanged for the same homologue from series-1 to series -X, which causes defense in the suitable magnitudes of anisotropic forces of intermolecular end to end attractions, commencement of mesophase, thermal stability, mesophase length range and other mesogenic properties.

CONCLUSIONS

A novel homologous series consisted of three phenyl rings and two ester central bridges which acts as rigid core and two end groups contributing flexible core of the molecules, induces nematic type of mesomorphism with absence of smectic property by less than 50% homologues. series is middle ordered melting type with high thermal stability. Group efficiency order derived on the basis of

(i) thermal stability (ii) commencement of mesophase (iii) total mesophase length for nematic with reference to molecular rigidity/flexibility are as under.

Nematic

- Rigidity/Flexibility: –CH=CH-COO-CH_2-Ph-OH(p) < -CH=CH-COO-CH_2-CH_2-Ph Suitable magnitudes of combined effect through molecular rigidity and flexibility can induce mesomorphism.

- Mesomorphism is very sensitive and susceptible to molecular structure.
- Present novel ester compounds may be useful in the study of binary systems and agricultural field.
- Presence of vinyl group is predominantly nematogenic.

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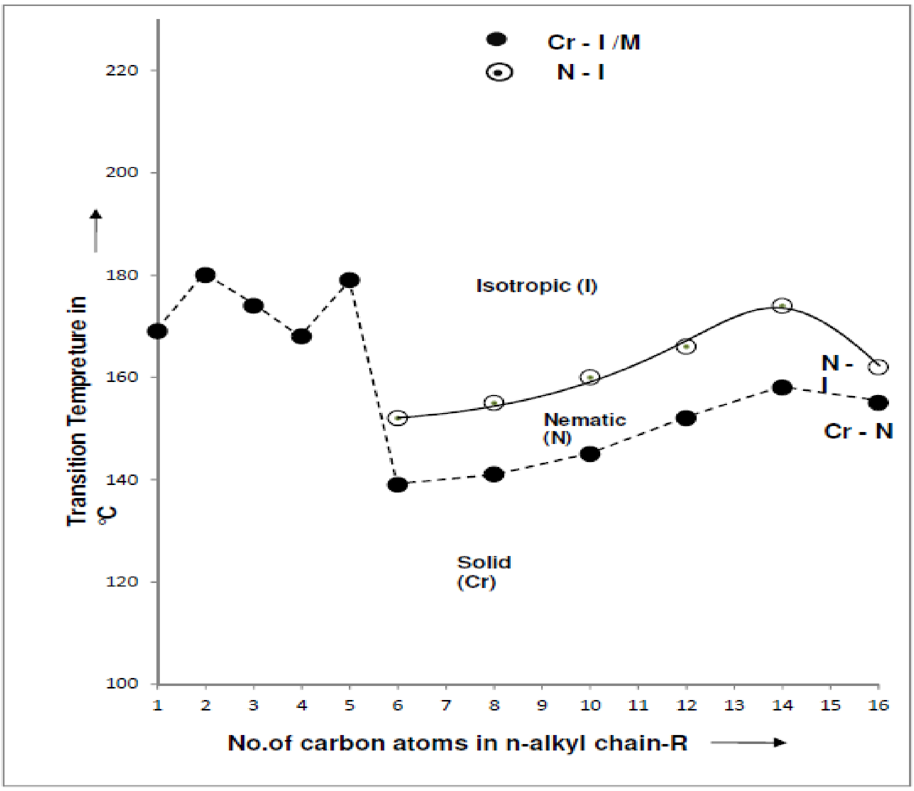

Figure: 1 Phase Behavior of Series.

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