

SYNTHESIS OF 4-HYDROXYBENZYL 4'-(4''-N-ALKOXY BENZOYLOXY) BENZOATE.

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Article Received on
09 April 2018,

Revised on 29 April 2018,
Accepted on 19 May 2018

DOI: 10.20959/wjpr201811-12398

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ABSTRACT

A Novel homologous series of mesogens have been synthesized and studied with a views to understand and establish the relations between molecular structure and liquid crystal properties of a Compounds. Totally eleven members of series synthesized. Mesogenic behaviors commences from C₆ member of a series and continued up to C₁₆ member. The rest of the members C₁ to C₅ are nonmesogenic. Mesogenic homologues (C₆ to C₁₆) are enantiotropically nematogenic. Textures of nematic phase are threaded or schlieren. Transition temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Analytical and structural data confirms

the molecular structures of homologues. Thermal stability for nematic is 195°C. Mesomorphic phase length range from 9.0°C to 33.0°C. Cr-I/N and N-I transition curves of a phase diagram behave in normal manner from C₁ to C₁₆ members. Mesogenic properties of present novel ester series are compared with the structurally similar series. Odd-even effect is missing for the N-I transition curve. Thus present series is partly nematogenic without exhibition of smectic property whose transition temperatures vary between 180°C and 205°C.

KEYWORDS: Liquid Crystal, Smectic, Nematic, Mesogen, Mesomorphism.

INTRODUCTION

Study of liquid crystalline (LC) state^[1] has attracted to the researchers belonging to science and technology, irrespective of their specialized branch of science or technology, with

different aims, objects and views^[2,3,4,5] in the benefit of mankind.^[6,7,8,9,10,11] Every researcher needs always novel substances to continue their research in their specialized objects. Therefore we being chemists decided to synthesize novel molecules which can yield novel thermo tropically mesomorphic (LC) substances. Number of LC substances have been reported^[12,13,14,15,16,17,18,19] till the date. However, proposed novel investigation is planned with a view to synthesise novel substances through homologous series consisted of two phenyl rings and one of the –COO– central groups. Thus, the present study will add some novel LC substances which can be useful to the researchers working in the field of Liquid crystals with different aims and objects. Thus, present study is aimed to synthesize novel LC substances to understand and establish the effects molecular structure^[20,21,22] on LC properties and evaluated data; will be interpreted in terms of molecular rigidity and flexibility.^[23,24,25,26]

Experimental: (Synthesis)

- P-n-alkoxy benzoic acids were prepared by the modified method of Dave and Vora (1970)^[27] using suitable alkylating agent (R-X).
- P-Hydroxy (4'-hydroxy benzyl) Benzoate was prepared by reacting P-Hydroxy Benzoic acid with corresponding p-Hydroxy benzyl alcohol (dissolve in Benzene) using modifying method of Doshi, Patel and Marathe through European pattern.^[28]
- Acid were directly condensed with the P-Hydroxy (4'-hydroxy benzyl) Benzoate dissolved in MDC in portions with DCC & DMAP as catalyst by stirring reaction mixture.^[29] Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. P-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, P-Hydroxy Benzoic acid, p-Hydroxy benzyl Alcohol, con. H₂SO₄, DCC, DMAP, MDC etc. required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in **Scheme -1**.

Table 4.5: Elemental analysis.

Compound	M. F.	Elements	%	Found	Elements	%	Calculated
		C	H	O	C	H	O
Propyl	C ₂₆ H ₂₃ NO ₇	70.93	5.46	23.62	71.01	5.58	23.22
Butyl	C ₂₇ H ₂₅ NO ₇	71.42	5.75	22.83	71.40	5.72	22.50
Pentyl	C ₂₈ H ₂₇ NO ₇	71.87	6.03	22.09	71.80	6.10	22.00

Spectral Data**IR (KBr) in cm^{-1} for Ethyl derivative (C-12).**

891 & 844 cm^{-1} para di substituted phenyl ring 1087,1045, 1244, cm^{-1} ether linkage, 1450,1625 cm^{-1} aromatic ring, 1728 cm^{-1} ester present, 2850, 2914 long chain alkane present, 3323 –OH Phenolic Present.

IR (KBr) in cm^{-1} for Decyl derivative (C-14).

891 & 844 cm^{-1} para di substituted phenyl ring 1008,1060, 1255, cm^{-1} ether linkage, 1450,1620 cm^{-1} aromatic ring, 1708 cm^{-1} ester present, 2850, 2924 long chain alkane present, 3323 –OH Phenolic Present.

 ^1H NMR (CDCl_3) in ppm for Propyl derivatives (C-03).

1.49 (t, 3H, –CH₃ of –OC₃H₇ group), 1.65 (m, 2H, methylene group of –OC₃H₇), 1.81 (t, 2H, Ar- O-CH₂), 5.60 (s, 2H, CH₂ of Ar-CH₂ –Coo), 6.92-7.27 (d, 4H, Ar-H), 7.29-7.45 (d, 2H, Ar-H), 7.54-7.92 (d, 2H, Ar-H), 8.06 - 8.22 (d, 4H, Ar-H), 9.24 (s, 1H, Ar-OH),

 ^1H NMR (CDCl_3) in ppm for Hexyl derivatives (C-16).

0.78-0.82 (t, 3H, –CH₃ of –OC₁₆H₃₃ group), 1.02-1.27 (m, 26H, polymethylene group of –OC₁₆H₃₃), 3.37-3.41 (m, 2H, Ar-(CH₂)₂O-CH₂), 3.44-4.20 (t, 2H, Ar-O-CH₂) 4.23 (s, 2H, CH₂ of Ar-CH₂ –Coo), 6.93- (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 7.44- (d, 2H, Ar-H), 8.20- (d, 1H, Ar-H), 9.28- (s, 1H, Ar-OH).

Table 2: Transition temperatures of 4-Hydroxybenzyl4'-((4''-n-alkoxy benzoyl)oxy) benzoate derivatives.

Sr. No.	n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	198
2	Ethyl	-	-	220
3	Propyl	-	-	189
4	Butyl	-	-	197
5	Pentyl	-	-	195
6	Hexyl	-	158	188
7	Octyl	-	160	180
8	Decyl	-	164	197
9	Dodecyl	-	182	202
10	Tetradecyl	-	190	205
11	Hexadecyl	-	189	198

RESULTS AND DISCUSSION

P- Hydroxy(4'-hydroxy benzyl) benzoate (yield 68 %) is a nonmesomorphic substance. But, on condensing it with n-alkoxy benzoic acid yielded C₆ to C₁₆ homologues as enantiotropic nematic without exhibition of smectogenic property. The rest of the homologues (C₁ to C₅) are nonmesogenic. Transition temperatures (**Table -2**) as determined from an optical polarizing microscopy with heating stage were plotted against the number of carbon atoms present in n-alkyl chain bonded with phenyl ring through oxygen atom of left flexible tail group. Like or related points were linked to draw Cr-I/N and N-T transition curves adopt a zigzag path of falling, rising and then falling with overall descending tendency up to C₁₂ homologue, then, it deviates at C₁₄ and C₁₆ homologues from usual expected behaviour. N-I transition curve initially rises and then descended as series is ascended up to C₁₀ homologue and then deviated from normal expected behaviors. i.e. it is first falling then rising and further falling for C₁₆ homologue. N-I transition temperature keeping in view of the trend of a N-I transition curve. The N- I curve is extended up to Cr – I (Isotropic) transition temperature. N – I transition curve does not exhibit odd- even effect. Mesogenic behaviors of liquid crystalline homologues vary from homologue to homologue in present series with changing number of methylene unit or units in flexible n- alkyl chain. Keeping alkyl tail group intact throughout the same series. The disappearance of n- alkoxy benzoic acids is due to the breaking of hydrogen bonding between two molecules of aromatic carboxylic acids by esterification process. The nonmesogenic property of homologues C₁ to C₅ members of a present series is attributed to their high crystallising tendency arising from inability of respective nonmesogenic homologues to resist externally exposed thermal vibrations as a consequence of unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole – dipole interactions and the low magnitude of dispersion forces by the interaction between instantaneous dipoles produce by the spontaneous oscillations of the electron clouds of the molecules which hinders the suitable magnitudes of anisotropic forces of intermolecular cohesion and disallows molecular arrangement required for definite range of temperature (i.e. zero temperature range). End to end attractions predominated more than lateral attractions. Therefore, more ordered sliding layered arrangement of molecules is less favored to facilitation formation of smectic phase against less bordered, statistically parallel orientational order of molecules in floating condition on the surface to cause nematogenic mesophase formation. Presently investigated novel series enhances nematic thermal stability and diminishes the stabilization of smectic mesophase formation. Absence of odd-even effect in N-I transition curve is attributed to the absence of mesophase forming tendency from C₁ to

C₅ homologues and absence of odd-even effect for higher homologues with longer n- alkyl chain which can be attributed to uncertainty in the status of relatively longer n- alkyl chain which may coil or bend or flex or couple to lie with major axis of core structure of molecules. Therefore intermolecular cohesive forces of C₁ to C₅ homologue are weakened to such an extent that, even, statically parallel orientation order of molecules C₁ to C₅ is not facilitated to cause nematic mesophase formation. Hence, reasons for nonmesomorphicity character of C₁ to C₅ are different. N-I transition curve is hypothetical and not realistic. Cr-I point is real which merges into isotropic point. The observed deviation behaviors transition curves for C₁₄ and C₁₆ can be attributed to longer n-alkyl chain and highly polar and polarizable and flexible nitro tail group which may have enthalpy value(H) unusually higher than normal of suitable magnitudes, which can exhibit mesophase formation in the normal condition. The variation in mesogenic properties of present series from homologue to homologue is due to the sequentially or progressively added -CH₂ - unit which added molecular polarization and length or size of each homologue molecule in the same series, keeping the rest of the molecular part unchanged. Thus, a series under discussion is partly nematogenic and partly nonmesogenic with absence of smectogenic character. The mesogenic behaviour of present series-1 are compared with structurally similar homologous series-X^[30] as shown in figure-2.

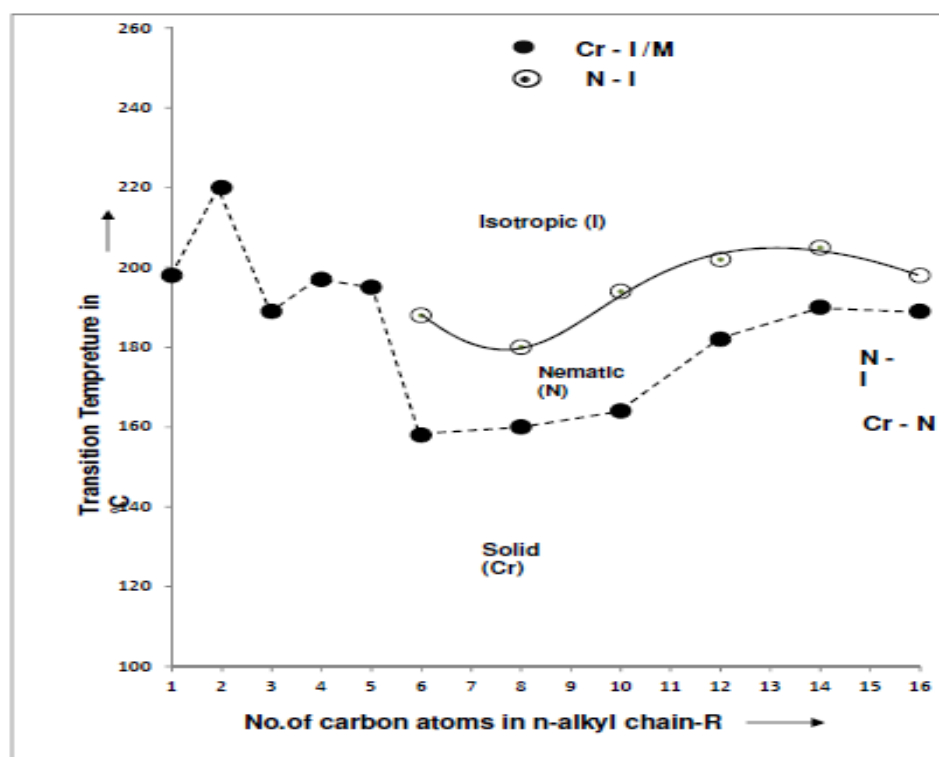


Figure 1: Phase Behavior of Series.

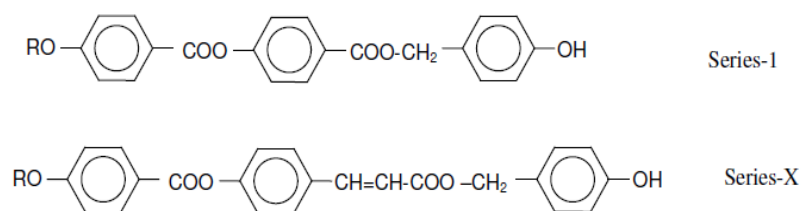


Figure 2: Structurally Similar Series.

Novel homologous series-1 and X are identical with respect to three phenyl rings and central bridge linking with both phenyl ring. Moreover left n-alkoxy flexible terminal end group C_nH_{2n+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 central bridge groups as and i.e. molecular rigidity differs but molecular flexibility remains unaltered. Homologous series-1 and X are identical with respect to central bridge linking middle and differs with respect to $-COO-CH_2-$ and $-CH=CH-COO-CH_2-$ 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	Series - 1	Series - X
Smectic -isotropic <u>Or</u> Smectic- nematic	-	-
Commencement of smectic phase	-	-
Nematic -isotropic commencement of nematic Phase	195°C (C_6-C_{16}) C_6	161.5°C ($C_6 - C_{16}$) C_6
Total mesophase length in °C (Nm-Iso)	9° - 33° C	7°C - 16°C
$C_{n_1} \quad C_{n_2}$	$C_{16} \quad C_{10}$	$C_{16} \quad C_{14}$

From above **table-3**, it is clear that,

- Presently investigated novel series -1 and X are only nematogenic.
- Nematic mesophase commences from C₆ homologue both of series-1 and X.
- Total Mesophase length range of series-1 is relatively higher 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 2 is a right terminal end -COO-CH₂, and -CH=CH-COO-CH₂-. Both central bridges contributes molecular rigidity of different magnitude though -COO-CH₂- unit as commonly present in Series 1 and X. The remaining uncommon part, other than -COO-common unit for series -1 and series -X respectively. The -CH=CH-COO-CH₂- unit of series-2 is longer than -COO-CH₂, group of series -1 which links with -COO- common unit of both series under comparison. However linking of uncommon longer unit -COO- bonded with common sp² hybridized -CH₂ unit through sp³ carbon of -CH₂, whereas the sp² carbon of shorter -COO-group of uncommon part of a central bridge of series - is bonded to a common sp² hybridized unit. Thus, longer and shorter differing units of present novel series-1 and X bonded with common tail unit -CH₂, through sp³ or sp² 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 difference 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.

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.

(i) Nematic

Rigidity/Flexibility: -COO-CH₂- > -CH=CH-COO-CH₂-

(ii) Nematic

Rigidity/Flexibility : -COO-CH₂- > -CH=CH-COO-CH₂-

(iii) Total (Sm+N):- (Right end group)

-COO-CH₂- > -CH=CH-COO-CH₂-

Series- 1

Series -X

- 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.

CONCLUSIONS

A novel homologous series consisted of three phenyl rings and two ester right end group which acts as rigid core and contributing flexible core of the molecules, induces nematic type of mesomorphism with absence of smectic property. Series is middle ordered melting type with high thermal stability.

ACKNOWLEDGEMENT

Authors acknowledge thanks to the S.P.T. Science College, Godhra for research facilities services as and when needed. Authors obliged to Dr. A. V. Doshi, Ex-Principal, M.V.M. Science College, Rajkot. Authors are also thankful to Dr. N.N. Vyas, Dr. V. R. Patel for their valuable helping hand and microscopic facility. Authors acknowledge thanks to Dept. of chemistry, Saurashtra University, Rajkot for analytical and spectral services.

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