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Synthesis and Evaluation of Liquid Crystal Behavior of a Novel Homologous Series :4-(4′-n-alkoxy benzoyloxy) –4”-Nitro Benzyl Benzoates

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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 substance. Totally eleven members of series synthesized. Mesogenic behaviors commences from C_5 member of a series and continued up to C_{16} member. The rest of the members C_1 to C_4 are nonmesogenic. Mesogenic homologues ($C_5$to C_{16}) are enantiotropically nematogenic without exhibition of smectic property. Textures of nematic phase are threaded or schlieren. Transition temperatures were determined by an optical polarizing microscopy (POM) equipped with a heating stage. Analytical, spectral and thermal data confirms the molecular structures of homologues. Thermal stability for nematic is 224.5 ºC. Mesomorphic phase length range from 6.0 ºC to 22.0 ºC. Cr-I/N and N-I transition curves of a phase diagram behave in normal manner from C_1 to C_{12} members and then higher members C_{14} and C_{16} deviated from normal behaviour. Mesogenic properties of present novel ester series are compared with the structurally similar series. Odd-even effect is observed for the N-I transition curve. Thus present series is nematogenic whose mesogenic transition temperatures vary between 185 ºC and 238 ºC. The present novel series is a middle ordered melting type and nematogenic, without exhibition of smectogenic character.

Key words: Liquid Crystal, Smectic, Nematic, Mesogen, Thermotropic.

INTRODUCTION

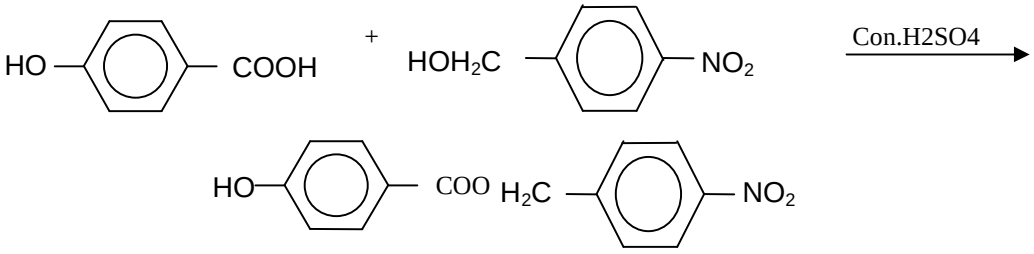
Study of liquid crystalline (LC) state [1] has attracted to the researchers belonging to science and technology, irrespective of their specialized branch of science or technology, with different aims , objects and views [2,3,4,5] in the benefit of mankind [6,7,8,9,10,11]. Every researcher needs always 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 three phenyl rings and one of the central groups –COO–CH_2– [20,21] which is novel and exploited by only Doshi-Patel and Marathe. 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 [22,23,24] on LC properties and evaluated data; will be interpreted in terms of molecular rigidity and flexibility [25,26,27,28].

MATERIALS AND METHODS

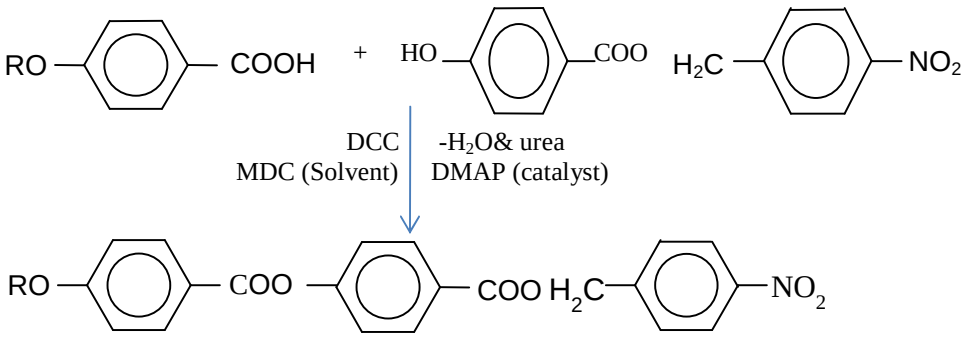
Experimental : (Synthesis)

- 4-n-alkoxy benzoic acids were prepared by the modified method of Dave and Vora [29] using suitable alkylating agent (R-X)
- 4-Hydroxy 4'-Nitro Benzyl Benzoates was prepared by reacting 4-Hydroxy Benzoic acid with corresponding 4-Nitro Benzyl Alcohol (dissolve in Benzene) using modifying method of Doshi, Patel and Marathe through European pattern.[30]
- Acids were directly condensed individually with the 4-Hydroxy 4'-Nitro Benzyl Benzoates dissolved in MDC in portions with DCC & DMAP as catalyst by stirring reaction mixture. [31] Products were decomposed ,filtered, washed, dried and purified, till the constant transition temperatures obtained. 4-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, 4-Hydroxy Benzoic acid, 4-Nitro Benzyl Alcohol, con. H_2SO_4 , 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**

(1) 4 – Hydroxy 4′-Nitro Benzyl benzoate



(2) 4-(4′-n-alkoxy benzoyloxy) –4"-Nitro Benzyl Benzoate



R = C_nH_{2n+1} n = 1,2,3,4,5,6,8,10,12,14,16

Scheme-1 Synthetic route to the series

Characterization :

Table -1 Elemental analysis for methyloxy, ethyloxy and propyloxy derivatives

Sr. No.	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
1.	$C_{22}H_{17}NO_7$	65.60 (64.86)	4.12 (4.17)	3.20 (3.23)
2.	$C_{23}H_{19}NO_7$	66.25 (65.24)	4.70 (4.49)	3.11 (3.00)
3.	$C_{24}H_{21}NO_7$	69.00 (66.20)	5.10 (4.82)	3.00 (2..91)

Spectral Data :
^{1}H NMR in ppmfor the Tetrayloxy derivatives : 1.2,1.3,1.5,1.6 (alkyl chain H), 3.8,3.6,4.08 (-OCH_2 of – OC_3H_7) , 7.2, 6.9(p-di substituted benzene ring and mono substituted benzene ring)

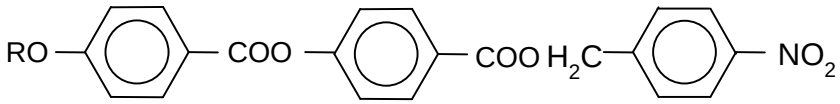
^{1}H NMR in ppmfor the Hexyloxy derivatives:1.2, 1.3,1.5,1.6,2.0 (alkyl chain H) 3.9, 4.0,4.06,(-OCH_2 of - OC_6H_{13}),6.8,7.2,,7.34(p-di substituted benzene ring and mono substituted benzene ring)

IR in cm^{-1}for Decyloxy derivatives : 891 & 844 cm^{-1} pera di substituted phenyl ring 1087,1045, 1244, cm^{-1} ether linkage, 1438,1512,16025 cm^{-1} aromatic ring ,1568,1344nitro group present,1728 cm^{-1} ester present, 2850, 2926 long chain alkane present

IR in cm^{-1} for Octyloxy derivatives : 893 & 842 cm^{-1} pera di substituted phenyl ring 1008, 1207, 1271 cm^{-1} ether linkage, 1442,1608 cm^{-1} aromatic ring ,1525,1305 nitro group present,1737 cm^{-1} ester present, 2866, 2941 long chain alkane present

Texture :by miscibility method;
Threaded nematic C_6
Schlieren nematic - C_{10} and C_{12}

Table-2 Transition temperatures

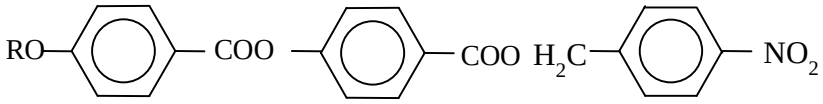


Sr. No.	n-alkyl Group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	240
2	Ethyl	-	-	227
3	Propyl	-	-	230
4	Butyl	-	-	226
5	Pentyl	-	226	232
6	Hexyl	-	217	230
7	Octyl	-	219	238
8	Decyl	-	219	226
9	Dodecyl	-	198	220
10	Tetradecyl	-	215	226
11	Hexadecyl	-	185	198

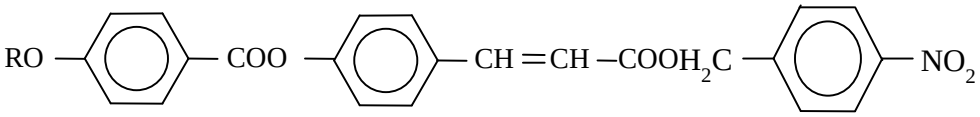
RESULTS AND DISCUSSION

4- Hydroxy-4'-nitro benzyl benzoate (MeltingPoint: 224, yield68 %) is a nonmesomorphic substance. But, on condensing it with dimerized n-alkoxy benzoic acid yielded C_5 to C_{16} homologues as enantiotropic nematic without exhibition of smectogenic property. The rest of the homologues (C_1 to C_4) are nonmesogenic. Transition temperatures (Table -1) as determined from an optical polarizing microscopy equipped with heating stage were plotted against the number of carbon atoms present in n-alkyl chain bonded to phenyl ring through oxygen atom of left flexible tail group. Like or related points were linked to draw Cr-I/N and N-I transition curves as shown in a phase diagram. Cr-N transition curve adopt a zigzag path of rising and falling with overall descending tendency. Then, N-I transition curve initially rises and than descended as up to C_{12} homologue in usual manner and then deviated from normal expected behaviors. i.e. it rises at C_{14} and descends at C_{16} in normal manner. Thus negligible deviation from normal behavior is observed at C_{14}. Very sharp and short odd- even effect is observed for N-I transition curve. 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`R` of –OR group. Keeping $–NO_2$ tail group intact throughout the same series. The disappearance of dimerization of n- alkoxy benzoic acids is due to the braking of hydrogen bonding between two molecules of aromatic carboxylic acids by esterification process. The nonmesogenic property of homologues C_1 to C_4 members of a present series is attributed to their high crystalising tendency arising from inability of respective nonmesogenic homologues to resist, externally exposed thermal vibrations

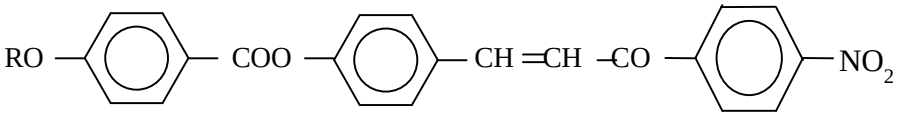
as a consequence of unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole – dipole interactions and the low magnitude of dispersion forces by the interaction between instantaneous dipoles produce by the spontaneous oscillations of the electron clouds of the molecules which 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). Highly polar and polarizable $-NO_2$ terminal situated as triled end group is high in the nematic order like –CN group, and low in the smectic order. $–NO_2$ group has strong dipole which lie along the long molecular axis. Such dipole giving repulsion between molecules which lie parallel to one another. i.e. side by side, and perpendicular to the layer planes of smectic liquid crystal. Thus, end to end attractions predominated more than lateral attractions. Therefore, more ordered sliding layered arrangement of molecules is less favored to facilitate formation of smectic phase against less bordered, statistically parallel orientational order of molecules in floating condition on the surface to cause nematogenic mesophase formation. Thus, $-NO_2$ end group present in the molecule of presently investigated novel series enhances nematic thermal stability and eliminates the stabilization of smectic mesophase formation. Very sharp and short odd-even effect diminishes in N-I transition curve is attributed to the absence of mesophase forming tendency from C_1 to C_4 homologues and then absence of odd-even effect for higher homologues with longer n- alkyl chain which can be attributed to uncertainty in the status of longer n- alkyl chain which may coil or bend or flex or couple to lie with major axis of core structure of molecules. The observed deviating behavior of N-I transition curve for C_{14} can be attributed to longer n-alkyl which curves uncertaintyin its status which modifies molecular rigidity and flexibility and varying enthalpy value(H)in manner. Unusually,The variation in mesogenic properties of present series from homologue to homologue is due to the sequentially or progressively added $-CH_2$ - unit which adds gradually molecular polarization and length and permanent dipolemoment across long molecular axes in the same series, keeping the rest of the molecular part unchanged. Thus, a series under discussion is 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] and Y [31] as shown in figure-2.



Series-1



Series-X



Series-Y

Figure : 2 Structurally Similar Series

Novel homologous series-1, x and y are identical with respect to three phenyl rings and central bridge linking first and middle 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, their tired group `R` of each series differs from homologue in the same series. The homlogus series 1,X and Y differs with respect to central bridges linking middle and third phenyl ring, i.e .molecular rigidity and flexibility together very for the same homologus from series to series wherever only molecular flexibility very from homologus to homologus in the same series due to –OR group.Thus, variations in mesogenic properties and the degree of mesomorphism observed, are depended upon the altering magnitudes of either molecular rigidity and/or the molecular flexibility among the presently investigated series-1 and the homologous series - X and Y 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 as a consequence of altering molecular rigidity or/and flexibility; as under.

Table-3 Average thermal stability in °C

Series	1	X	Y
Smectic- Isotropic or smectic- Nematic commencement of smactic phase	–	–	125.6 (C_6-C_{14}) C_6-
Nematic-Isotropic commencement of nematic phase	224.3 (C_5-C_{16}) C_5	198.0 (C_6-C_{14}) C_6	154.6 (C_3-C_{16}) C_3
Mesophase length range in °C from (Nm+I) $C_n\alpha$ to $C_n\beta$	06 - 22 C_5 C_{12}	11 - 50 C_6 C_{14}	18 - 73 C_3 C_8 C_{16}

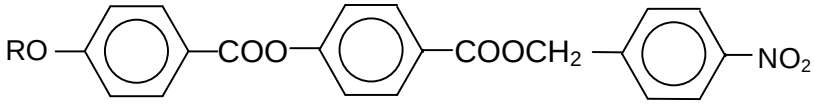
From above table-3, it is clear that,

- Presently investigated novel series -1 and X are only nematogenic whereas series -Y is nematogenic us smectogenic
- Smectic property commences from C_6 homologue of a series -Y, whereas, it does not commence till the last member of a series X and S 1.
- Nematic mesophase commences from C_5 homologue of series-1 whereas it commences from C_6 and C_3 homologue of the series X and Y respectively.
- Total Mesophase length range of series-1 is relatively lower than series- X and Y.

Mesogenic characteristics difference of a substance varies with changing structural part of a molecules due to chaning features of moleculer rigidity and flexibility under comparison. The changing molecular structural part between series-1 ,X and Y are central bridge, -COO-CH_2- , - CH=CH-COO-CH_2- and-CH=CH-CO- and tailed ends.

central bridges contributes molecular rigidity of different magnitude though common -CH=CH- unit series X and Y present.. The remaining uncommon part, other than -CH=CH- common unit are - COO-CH_2- for series -1 and –CO- for series -Y respectively. The–$COOCH_2$--unit of series-1 is longer than –CO- group of series -Y which links with -C_6H_4-NO_2 common unit of all series under comparison. However linking of uncommon longer unit –COO-CH_2- bonded with common sp^2 hybridized -C_6H_4 -NO_2 unit through sp^3 carbon of -CH_2, whereas the sp^2 carbon of shorter –CO-group of uncommon part of a central bridge of series -Y is bonded to a common sp^2 hybridized -C_6H_4-NO_2 unit. Thus, longer and shorter differing units of present novel series-1 and X bonded with common tail unit -C_6H_4-NO_2, through sp^3 or sp^2 carbon respectively. Such differences induces differing feature into molecular polarity and polarizability as a consequence changing 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.

Homologous Series: **4-(4′-n-alkoxy benzoyloxy) –4”-Nitro Benzyl Benzoates”**



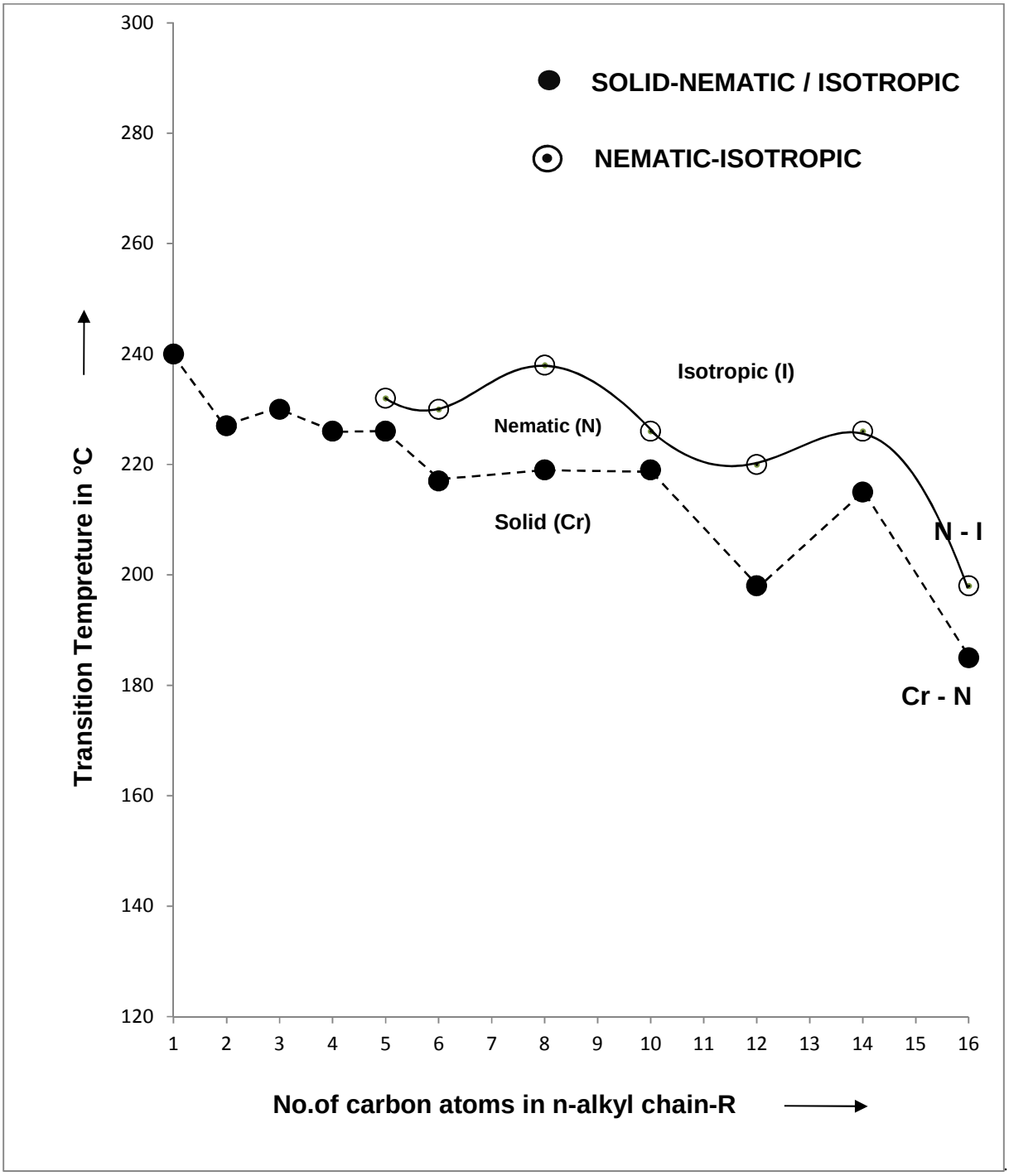


Figure :1 Phase Behavior of Series

CONCLUSION

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. It is a higher middle ordered melting type series with high thermal stability.

Group efficiency order derived on the basis of
(i) thermal stability (ii) commencement of mesophase (iii) total mesophase length for smectic and nematic with reference to molecular rigidity/flexibility are as under

(i) Smectic:
Rigidity/Flexibility : -CH=CH-CO - >-COO-CH_2- = -CH=CH-COO-CH_2-
Nematic
Rigidity/Flexibility : -COO-CH_2- > -CH=CH-COO-CH_2 - > - CH=CH-CO-

(ii) Smectic:
Rigidity/Flexibility : - CH=CH-CO- >-COO-CH_2- = -CH=CH-COO-CH_2-
Nematic
Rigidity/Flexibility : - CH=CH-CO- >-COO-CH_2- > - CH=CH-COO-CH_2-

(iii) Total (Sm+N):- (Central group)
- CH=CH-CO- >-CH=CH-COO-CH_2->-COO-CH_2-

- 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 production.
- Presence of vinyl group is predominantly nematogenic.

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