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Synthesis of a novel liquid crystalline ethylene derivatives of a series: α-4-[4'-n-alkoxy benzoyloxy] phenyl-β-3"-nitro benzoyl ethylenes

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ABSTRACT

Titled homologous series is predominantly mesogenic and partly nonmesogenic. Ethoxy to hexadecyloxy homologues are mesogenic while only methoxy derivative of a series is nonmesogenic. Ethoxy to butyloxy and hexadecyloxy homologues are only nematogenic while rest of the mesogenic homologues exhibit smectogenic character in addition to nematogenic character.Odd-even effect and alternation of transition temperature observed for nematic -isotropic transition curve and solid-isotropic or smectic-nematic transition curve in a phase diagram. Transition temperatures and other liquid crystal properties were observed through a hot stage polarizing microscope. Analytical data support the molecular structures of homologues. Textures of nematogenic homologues are threaded or schilieren and that of smectic phase are focal conic fan shaped of smectic-A type.Smectic and nematic thermal stabilities are 121.2^{0}C and 160.0^{0}C respectively. Liquid crystal properties of the series are compared with a structurally similar homologous series.

Key words: Liquid crystal, Mesogenic, Nematic, Smectic, Mesogen

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INTRODUCTION

Synthesis of a new homologous series of liquid crystal (LC) materials by varying molecular rigidity and/or flexibility is an important tool. Variations of molecular rigidity and/or flexibility can be brought about by changing molecular shape, size, aromaticity, width, polarity, polarizability etc. including variation of lateral, terminal and central group or groups. Presently, a homologous series consisted of three phenyl rings linked through –COO- and –CH=CH-CO- central bridges as rigid core and flexible core is left n-alkoxy end group and meta substituted nitro lateral group to –CH=CH-CO- group. Titled homologous series of eleven homologues planned to form by varying n-alkyl group of left n-alkoxy terminal keeping –NO_2 group unchanged. Thereby, a new series will be evaluated and discussed in terms of the relation between molecular structure and liquid crystal properties based on molecular rigidity and flexibility.

MATERIALS AND METHODS

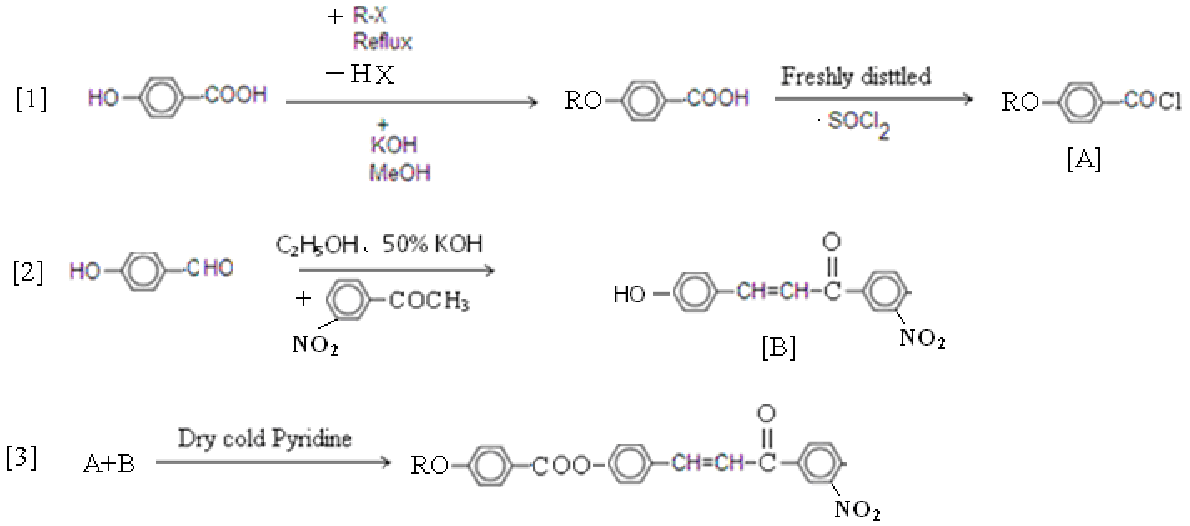
Synthesis

4-Hydroxy benzoic acid was alkylated by suitable n-alkyl halide. Then n-Alkoxy benzoic acids were converted to corresponding n-alkoxy benzoyl chloride (A) using thionyl chloride by modified method of Dave and Vora [4]. α-4-

Hydroxyphenyl-β-3' nitro benzoyl ethylene (B) was prepared by usual established method [6c]. Components (A) and (B) were condensed in dry cold pyridine. 4-Hydroxy benzoic acid, KOH, CH_3OH, n-Alkyl halides, thionyl chloride, pyridine, m-nitro acetophenon, 4-hydroxy benzaldehyde,C_2H_5OH etc. required for synthesis of analar quality were used as received. Synthetic route to the series is mentioned in scheme-1

Characterization:

Selected number of representative homologues were characterized by elemental analysis, Infrared (IR) and ^{1}HNMR spectroscopy. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer as shown in table-1. IR spectra were recorded on Perkin-Elmer spectrum GX. ^{1}HNMR spectra were recorded using $CDCl_3$ as solvent. Liquid crystal properties were determined by an optical polarizing microscopy equipped with heating stage. Texture of nematic and smectic phase were determined by miscibility method. Thermodynamic quantities enthalpy(ΔH) and Entropy (ΔS) discussed qualitatively instead of DSC scane.



Scheme -1 synthetic route to the series

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

Table: 1 Elemental analysis for Propyloxy,Butyloxy, Pentyloxy and Tetradecyloxy derivatives

Molecular formula	Element % found (% calculated)		
	C	H	N
$C_{25}H_{21}NO_6$	69.51 (69.60)	4.84 (4.87)	3.39 (3.25)
$C_{26}H_{23}NO_6$	70.23 (70.11)	5.16 (5.17)	3.23 (3.15)
$C_{27}H_{25}NO_6$	70.42 (70.59)	5.43 (5.45)	3.00 (3.05)
$C_{36}H_{43}NO_6$	73.98 (73.85)	7.43 (7.35)	2.48 (2.39)

Analytical data:

NMR in PPM for Octyloxy derivative:

0.801 ($-CH_3$ of OC_8H_{17}),1.2459 ($(-CH_2-)_n$ of OC_8H_{17}),4.02 (Triplet-OCH_2-CH_2),6.9 (broad) (-CH=CH-),6.93 to 8.1 (m ,p-sub.Phenyl ring)7.21 –CH=CH-CO- NMR confirms the structure.

NMR in PPM for Dodecyloxy derivative:

.875($-CH_3$ of $OC_{12}H_{25}$)1.258 ($(-CH_2-)_n$ of $OC_{12}H_{25}$) 4.01(Triplet-OCH_2-CH_2 of $OC_{12}H_{25}$) 4.72(broad) (-CH=CH-) 6.89to 7.93(m ,p-sub.Phenyl ring)6.91–CH=CH-CO- NMR confirms the structure.

IR in Cm^{-1} for Hexyloxy derivative:

650& 700 (m-sub. Phenyl ring) ,850 (p-sub. Phenyl ring), 1160 (C-O of alkoxy-OC_6H_{13}), 1440 ($-NO_2$ group),1250 ,1610,1680 (-COO-group)-940 (-CH=CH-) 700(polymethelyne of C_6H_{13}) IR confirms the structure.

IR in Cm^{-1} for Decyloxy derivative:
690&760(m-sub. Phenyl ring), 840 (p-sub. Phenyl ring).1160 (C-O of alkoxy-$OC_{10}H_{21}$), 1020(-CH=CH-)1260&1600(-COO group), 1480 (-NO_2 group) 720 polymethelyne of $C_{10}H_{21}$ IR confirms the structure.

Texture by miscibility method

Homologue	**Texture**
• Butyloxy derivative	Threaded
• Hexadecyloxy derivative	Schlieren
• Octyloxy derivative	Smectic- A
• Dodecyloxy derivative	Smectic- A

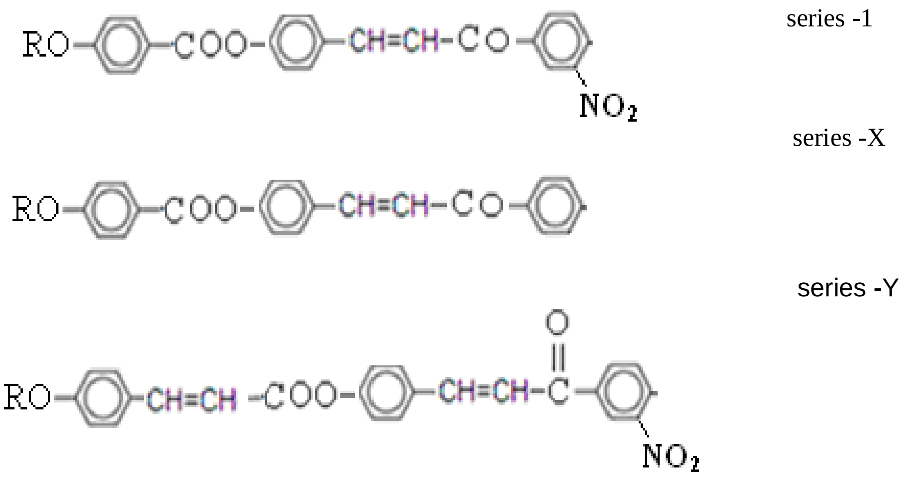


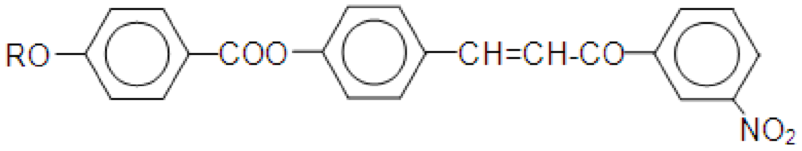
Figure: 2 structurally similar series

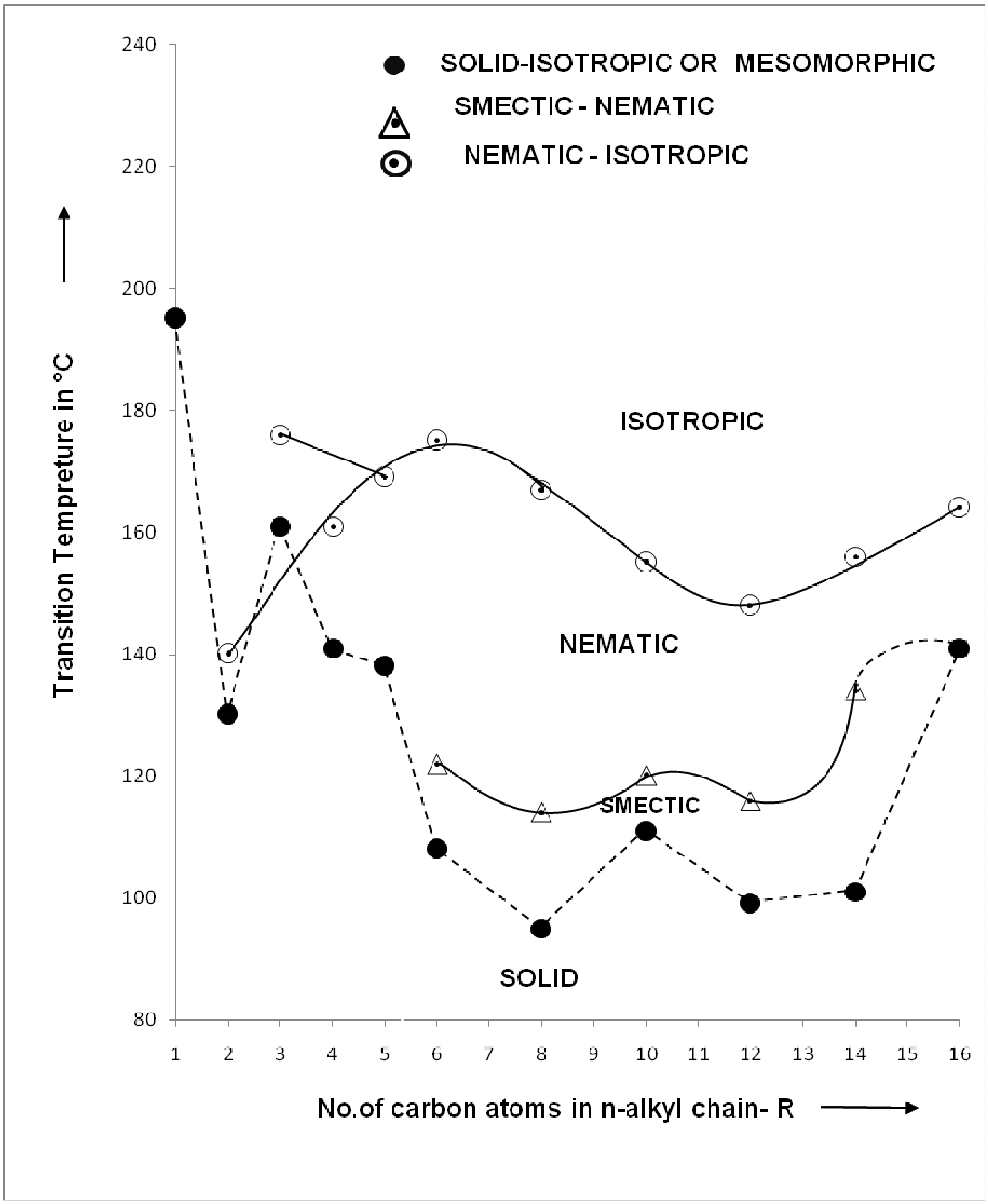
Table -2 Transition temperatures of series in °C

Sr.no	n-alkyl group -C_nH_{2n+1}	Transition temperatures in °C		
		Sm	Nm	Isotropic
1	1	-	-	195.0
2	2	-	130.0	140.0
3	3	-	161.0	176.0
4	4	-	141.0	161.0
5	5	-	138.0	169.0
6	6	108.0	122.0	175.0
7	8	95.0	114.0	167.0
8	10	111.0	120.0	156.0
9	12	99.0	116.0	148.0
10	14	101.0	134.0	156.0
11	16	-	141.0	164.0

Sm- Smectic Nm-Nematic

Homologous Series: α-4-[4’-n-Alkoxy Benzoyloxy] benzoyl-β-3’’- Nitro phenyl – ethylenes.





RESULTS AND DISCUSSION

Alkoxy benzoic acids are dimerized by hydrogen bonding. Hydrogen bonding breaks on esterification on linking it with α-4-hydroxy phenyl β-3'-nitro benzoyl ethylene. Keto ester formed consisted of three Phenyl rings bridged through carboxy –COO- and vinyl keto–CH=CH-CO- central groups. Eleven keto esters formed were observed through hot stage Polarizing microscopy. Ethoxy to hexadecyloxy derivatives were liquid crystals while only one i.e. methoxy derivative was found nonliquid crystal. Hexyloxy to tetradecyloxy derivatives exhibit enantiotropically smectogenic characteristic in addition to enantiotropically nematogenic characteristic. Rest of the liquid crystalline homologues exhibit only enantiotropic nematic mesophase. A phase diagram representing phase behavior of the series (figure1) drawn by joining like points for the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group versus the transition temperatures of homologues and recorded in table-2.solid-isotropic or mesomorphic transition curve adopts a zigzag path of rising and falling as series is ascended with overall falling tendency. Smectic-nematic transition curve propagate in serpantile shape in alternatively rising and falling manner; without odd –even effect. This curve is extrapolated[6e] to hexadecyloxy homologue to predict hypothetically a probable latent transition temperature [LTT] for smectic following the trend of a curve. A solid- nematic transition temperature practically observed and LTT predicted hypothetical for smectic- nematic coinsided. i.e 141-141=0 , means smectic-nematic phase length zero or practically no smectic phase occurred in reality by hexadecyloxy homologue. Nematic-isotropic transition curve initially rises and then falls upto dodecyloxy homologue and again rises from and beyond dodecyloxy derivative with odd-even effect. Thus, nemetic-isotopic transition curve also adopts serpantile shape of is propagation. Nonliquid crystalline behavior of methoxy derivative is due to its high crystallising tendency arising from its shortest n-alkoxy chain length which strengthens intermolecular attractions and shows its inability of resisting thermal vibrations exposed upon it. As a result of this, it sharply melts at its melting point to isotropic liquid without passing through liquid crystal state. Exhibition of smectogenic property by hexyloxy to tetradecyloxy homologues of the series is attributed to their lamellar packing of molecules in their crystal lattices due to the presence of laterally meta substituted highly polar nitro group and increased molecular polarizability as a consequence of molecular broadening which exceeds, magnitudes of anisotropic forces of intermolecular attractions as compared to opposing forces caused due to molecular widening[5]. As a result of this, molecules concern are able to resist thermal vibrations exposed upon them from external source called, thermodynamic surroundings and molecules float with sliding layered arrangement with restricted two dimensional order of disorder or entropy $(\Delta S) = \Delta H/T$. The exhibition of nematogenic mesophase formation by homologues except methoxy derivative is attributed to the molecular disalignment at an angle less than 90^0 on the plane of a surface due to the suitable magnitudes of anisotropic intermolecular forces of attractions which maintains statistically parallel orientational order of molecules in floating condition, resisting exposed thermal vibrations; within definite range of temperature reversibly. Molecules of homologues randomly orient in all possible directions beyond isotropic temperature with high order of disorder or entropy(ΔS). Molecular rigidity and flexibility[1,2,3] are varied with rising or falling of temperature controlling magnitudes of anisotropic forces of intermolecular attractions against applied heat. The variation of mesomorphic behavior from homologue to homologue and odd-even effect is attributed to the sequencially added methylene unit to the left n-alkoxy terminal end group keeping $–NO_2$ group intact. The mesomorphic behavior and the degree of mesomorphism of presently investigated series (1) are compared with structurally similar homologous series (X)[6a] and (Y)[8] as shown in figure 2.Table 3 represents average thermal stability and commencement of mesophase

Series 1 and X are identical in all respect except meta substituted $-NO_2$ group linked at the third phenyl ring which replaces –H of third phenyl ring of series X. Series -1 and Y are identical in all respect except central bridge –COO- and –CH=CH-COO-[7] respectively. Therefore observed variations in liquid crystal behaviors are attributed to their varied central or terminal/lateral group of different rigidity –flexibility and polarity or polarizability.

Table 3 : Average Thermal Stability

Series	**Average transition temperatures in ^{0}C**		
	Series (1)	**Series(X)**	**Series(Y)**
Smectic-Nematic	121.2 (C_6-C_{14})	106.6 (C_{10}-C_{14})	154.6 (C_5-C_8)
Commencement of smecticphase	C_6	C_{10}	C_5
Nematic-isotropic	160.0 (C_2-C_{16})	119.8 (C_8-C_{16})	163.8 (C_5-C_{16})
Commencement of Nematic mesophase	C_2	C_8	C_5

Table 3 indicates that smectic and nematic thermal stabilities of series-1 are relatively higher than the corresponding series-X which differes by only –NO_2 group.Meta substituted-NO_2 group widens or broadens a molecule of series 1 as compared to the molecules of series -X. Therefore intermolecular closeness of series- X is more than the series-1. This closeness factor may increase magnitudes of intermolecular adhesion of series X which is more than series 1. But, at the same time increased molecular width increases molecular polarizability and hence the intermolecular attractions enhancs. Thus two opposing effects operated at a time, in which second effect due to increased polarizability predominates to intermolecular closeness effect.

Therefore, smectic-nematic and nematic-isotropic thermal stabilities of series-X exceed the same of series -1 of present investigation. On comparing thermal stability for smectic of series -1 is lower than the series-Y, but nematic thermal stabilities of series-1(160.0) and series-Y (163.8) are equivalent or nearly equivalent. Both series-1 and Y contain meta substituted –NO_2 group on third phenyl ring but they differ in their first central group –COO- and –CH=CH-COO- respectively. Thus, both these central bridges are comparable through the vinyl carboxylate –CH=CH-COO- has greater length by –CH=CH- unit and causes more noncoplanarity due to a twist obtained as the oxygen atom of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings. Moreover greater length of –CH=CH-COO- by –CH=CH- unit increases length to breadth ration in comparision with –COO- group. Thus, extent of noncoplarity and intermolecular attraction due to –CH=CH-COO- of series y will be greater than the –COO- central group of presently investigated series. This greatness of –CH=CH-COO- group strengthens anisotrpic forces of attraction, a hence the lamellar packing of molecules of series y. Therefore, the smectic–nematic thermal stability of series y is greater than the corresponding series -1 keeping nematic-isotropic thermal stability almost equivalent or a little bit more by 3.8 unit (163.8-160.0) in comparision with series -1 .The smectic phase commences from sixth homologue in series -1, while it commences from fifth homologue in case of series y . However , smectogenic mesophase formation prolog upto tetradecyloxy homologue in series -1 in comparision with series y in which smectic phase prolongs upto octyloxy derivative.Nematic mesophase commences from second homologue to last hexadecyloxy homologue in series 1 while, it commences to appear late from fifth homologue to hexadecyloxy homologue in series y. Thus, smectic phase stabilizes at the cost of nematic phase in case of series y. The mesomorphic phase length varies between 10^o C to 72^o C at ethoxy and octyloxy homologues respectively. Thus series under present investigation is predominantly nematogenic and partly smectogenic with good wide range of mesomorphism and middle order melting type . Variations in mesogenic properties for same homologue from series to series is attributed to the laterally substituted –NO_2 and –H group of fixed polarity and central groups –COO- and –CH=CH-COO- .Which alters molecular polarity, rigidity and flexibility.

CONCLUSION

(1) Present series 1 is predominantly nematogenic and partly smectogenic with middle ordered melting type.
(2) Molecular rigidity alters by central bridge or bridges and the member of phenyl rings.
(3) Molecular flexibility is altered by lateral and/or terminal end groups.
(4) Smectic mesophase stabilizes at the cost of nematic phase in a homologuus series containing vinyl carboxylate group.

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