Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2011, 3 (5): 185-190
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis and study of Ester Mesogenic Homologous Series: Ethyl-o-[p'-n-alkoxy benzoyloxy]benzoates

Doshi A.V.*, Joshi C.G.[a] and Bhoya U. C.[b]

**Matushri Virbaima Mahila Science & Home Science College, Rajkot(Gujarat-India)*
[a]Chemistry Deptt., M. D. Science College Porbandar, (Gujarat India)
[b]Department of Chemistry, Saurastra University, Rajkot(Gujarat-India)

ABSTRACT

Ester homologous series Ethyl-o-[p'-n-alkoxy benzoyloxy]benzoates was synthesized by condensing p-n-alkoxy benzoyl chloride with o-hydroxy ethyl benzoates in pyridine. Work was planned to synthesize new liquid crystal material with a view to understand the effect of structural variation on liquid crystal [LC] or mesogenic character. Series consists of eleven homologues in which butyl to hexyl, octyl, decyl derivatives are enantiotropically nematogenic only, dodecyl derivative is enantiotropic Smectic in addition to nematogenic character, tetradecyl and hexadecyl derivatives are enantiotropic smectic only. Phase behaviour and mesogenic properties are determined from phase diagram drawn from the transition temperatures of the homologues observed using hot stage polarizing microscope. Texture of nematic mesophase is threaded or schlieren type and that of the smectic mesophase is focal conic fan shaped of A or C type. Mesophase length ranges from 5.0 °C to 44.0 °C with middle ordered melting type. Analytical data support the structure. Mesogenic properties are compared with structurally similar homologous series.

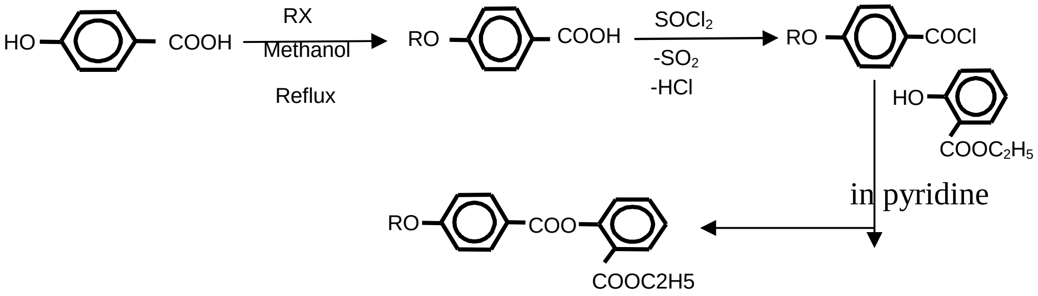
Keywords : Liquid crystal, Mesogens, Nematic, Smectic, Monotropic.

INTRODUCTION

Benzoates and Cinnamates derivatives are biologically and pharmaceutically bioactive molecules are being useful for medical and analytical fields. Moreover liquid crystal property of ester or other homologues can be exploited and used for LCD computer, television or other electronic screens and electronic display devices at desired temperature. Thus one should have knowledge of relation between liquid crystallinity and molecular structure to predict the molecular geometry, type of groups linked at suitable position and their polarity etc. Present work was planned and studied for the purpose mentioned above.

MATERIALS AND METHODS

Experimental: Alkylation of p-hydroxy benzoic acid and p-n- Alkoxy benzoyl chloride from corresponding n-alkoxy benzoic acids were prepared by modified method of Dave and Vora [3]. o-Hydroxy Ethyl benzoate was prepared by usual established method [4,8]. Eleven esters were synthesized by condensing Equimolar proportion of p-n- alkoxy benzoyl chloride and o-hydroxy Ethyl benzoate in pyridine. Products were decomposed, filtered, washed, dried and purified by alcohol till constant transition temperatures were obtained. P-hydroxy benzoic acid, o-hydroxy benzoic acid, Alkyle halide, Methanol, Thionyl chloride, Pyridine, Ethanol, KOH, H_2SO_4 were used as received. The synthetic route of the series is mentioned below in schem-1.



Where R= C_nH_{2n+1}, *n= 1 to 6, 8, 10, 12, 14, 16*

SCHEME-1: Synthetic route to the series

Characterisation

Selected representative homologues were characterized by IR spectra, elemental analysis. Thermodynamic quantities energy content (ΔH) and entropy (ΔS) values with reference to thermal stability of homologues and series are discussed qualitatively without performing DSC scane. Mesogenic textures were recognized by miscibility method using hot stage polarizing microscope.

Analytical data:

TABLE: 1 Elemental analysis for Propyloxy, Decyloxy and Tetra Decyloxy derivatives

Sr.No.	Molecular formula	Elements % Found (% Calculated)	
		C	H
1	$C_{19}H_{20}O_5$	69.43 (69.51)	6.27 (6.10)
2	$C_{26}H_{34}O_5$	73.31 (73.24)	8.05 (7.98)
3	$C_{30}H_{42}O_5$	74.96 (74.68)	8.60 (8.71)

IR Spectra in cm^{-1} for Butaloxy derivative

n- Butyloxy derivative: 750cm^{-1} polymethylene of C_4H_9, 840 cm^{-1} p-sub. benzene ring, 1160, 1250 & 1780 cm^{-1} ester group, 2900 cm^{-1} satu. C-H str. of alkyl, 3000 cm^{-1} aro. =C-H str. of phenyl.

Miscibility Method:

Pentyloxy and octyloxy derivative: Threaded type Nematic
Dodecyloxy derivative: Smectic – A

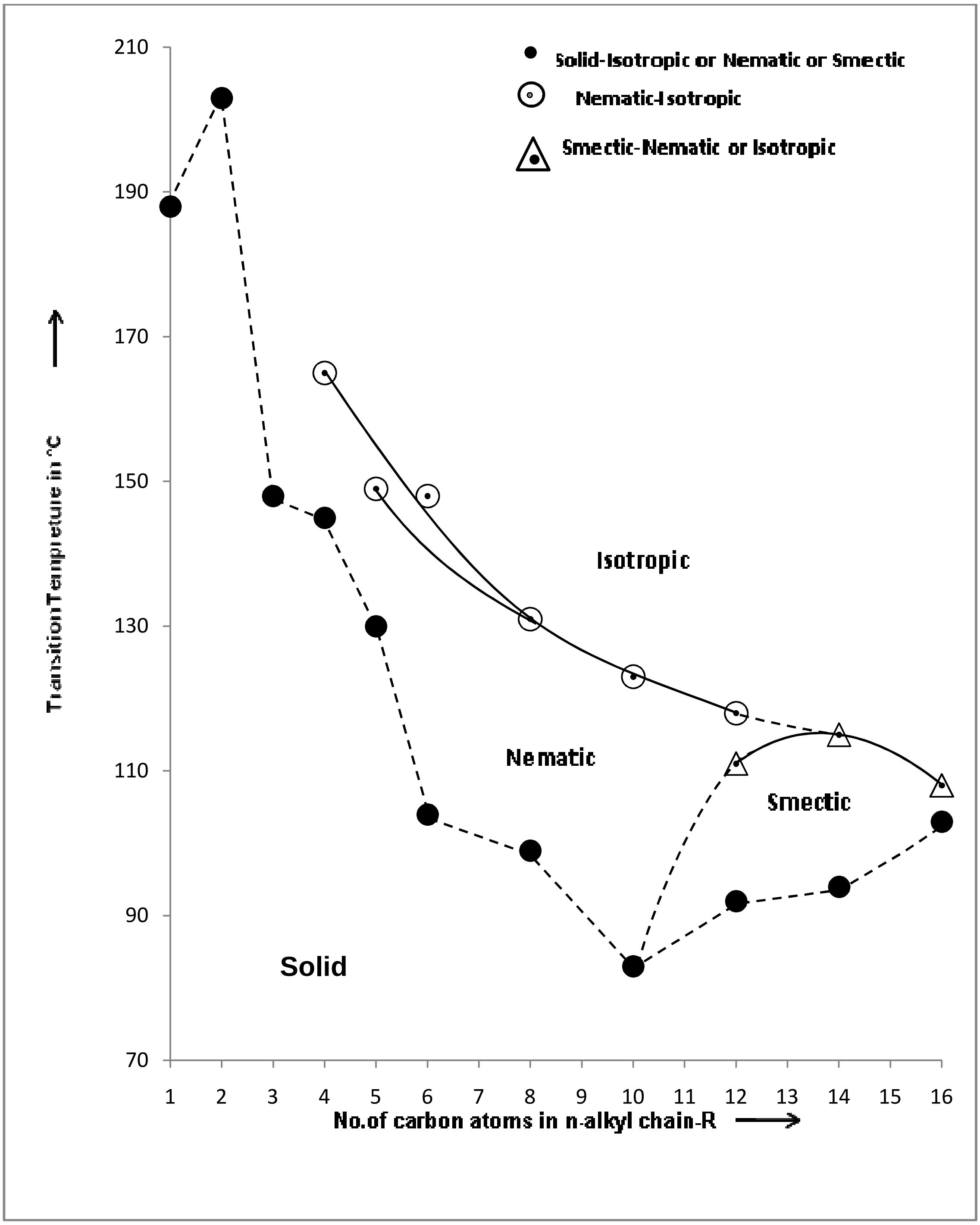


Figure:1 Phase behavior of the series
Series: Ethyl-o-[p'-n-alkoxy benzoyloxy] benzoates

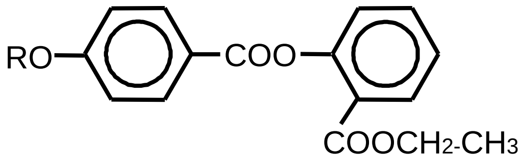
RESULTS AND DISCUSSION

Titled homologous series consists of eleven homologues which exhibits mesogenic property for eight homologues viz. Butyl to hexyl, octyl, decyl derivatives as only enantiotropic nematic, dodecyl derivative as polymesomorphic, and tetradecyl and hexadecyl derivatives as only enantiotropic smectogenic. Methyl, Ethyl and Propyl derivatives are nonmesogenic. Nematic mesophase is of threaded or schlieren textured and smectic mesophase is focal conic fan shaped of smectic - A or C variety. Microscopic observations are recorded in table-2. Phase diagram for a series are plotted for the transition temperature [Table-2] against number of carbon atoms in n-alkyl chain of left alkoxy terminally situated end group as shown in figure-1. Looking to the phase behaviour from figure-1, The solid isotropic or nematic or smectic transition curve follows a zigzag path of rising and falling with overall falling tendency as series is ascended. Smectic-nematic or isotropic transition curve rises and falls after passing through maxima in usual manner, and Nematic-isotropic transition curve shows descending tendency as series is ascended with persistence of uncleared odd-even effect. Nematic-isotropic transition curve merges into smectic-isotropic transition curve at tridecyl homologue on extrapolation. Similarly smectic-isotropic transition curve on extrapolation merges into decyl derivative, predicting its inability of showing smectogenic character.

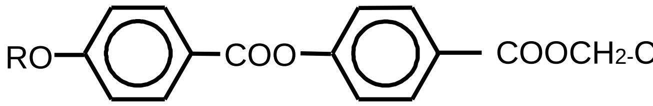
TABLE-2 Transition temperatures in ^{o}C of series

Compound No.	R=CnH2n+1 (n)	Sm	Nm	Isotropic
1	1	-	-	188.0
2	2	-	-	203.0
3	3	-	-	148.0
4	4	-	145.0	165.0
5	5	-	130.0	149.0
6	6	-	104.0	148.0
7	8	-	99.0	131.0
8	10	-	83.0	124.0
9	12	92.0	111.0	118.0
10	14	94.0	-	115.0
11	16	103.0	-	108.0

Nonmesogenic compound o-hydroxy Ethyl benzoate on condensation with dimeric p-n-alkoxy benzoic acids through acid chloride gives rise to ester homologues of relatively lower transitions because of the disappearance of hydrogen bonding of p-n- alkoxy benzoic acid by esterification. Nonmesogenic behaviour of methyl, ethyl and propyl homologue derivatives are attributed to their high crystallizing tendency arising from their thermodynamical high stability as a consequence of higher magnitude of intermolecular attractions and rigidity. Uncleared odd-even, effect alternation of transition temperatures and variation of mesogenic or liquid crystal property from homologue to homologue in the same series are attributed to the sequentially and progressively added methylene unit in the left n- alkoxy terminal end group. Table-3 summaries average thermal stability and molecular structure of the present series-1 and other structurally similar homologous series A [4] chosen for comparative study with respect to mesogenic property as shown in figure-2.



Series-1



Series-A

The homologous series-1 and A contain two phenyl rings bridged through carboxy –COO- central group and left n- alkoxy terminal end group as common identical geometry but they differ in same substituted group positioned at second phenyl ring. A common substitute –COOH$_2$-CH$_3$ group is positioned at ortho position to the central group in series-1, while it is positioned at para position to central group in case of series-A. Thus rigidity and molecular flexibility, intermolecular distance, molecular polarity and polarizability, length to breadth ratio, anisotropic forces of intermolecular attractions of suitable magnitude to induce liquid crystal property, thermal stability etc. vary from series-1 to A.

TABLE-3: Average Thermal Stability in ^oC

Series	1	A
Smectic-Nematic Or Isotropic	111.3 [C_{12}-C_{16}]	89.0 [C_6-C_{12}]
Nematic-Isotropic	139.1 [C_4-C_{12}]	-
Commencement of smectic mesophase	C_{12}	C_5

Laterally substituted –$COOCH_2$-CH_3 widens the molecules while para substituted –$COOCH_2$-CH_3 increases molecular length. Thus ratio of the molecular polarity to polarizability vary from series 1 to A. Hence thermodynamically quantum of heat content [ΔH] associated with molecules of series-**1** and **A** differ. As homologue sample molecules are observed through polarizing microscope with simultaneous heating or cooling from or to surroundings, the heat content [ΔH] linked with intermolecular forces of attraction of a sample molecular system is affected positively or negatively depending upon heat supplied from or to the surrounding or system.

Thus ratio of the $\Delta H/T$ i.e. $\Delta S= \Delta H/T$ varies accordingly. ΔS is called the entropy change or molecular randomness or magnitude of molecular disorder within the bulk of molecular thermodynamic system. Molecules of a sample homologue may adopt statistically parallel orientational ordered arrangement or/and sliding layered molecular arrangement under the influence of anisotropic forces of attractions environment in floating condition. Hence, nematic and/or smectic mesophase appear during microscopic observation. Enisotropic environment under the influence of heat supplied from or to the surroundings within definite range of temperature of a thermotropic liquid crystal substance, which is called phase length or ‘degree of mesomorphism’ or ‘liquid crystallinity’. Homologous series-1 is predominantly nematogenic and partly smectogenic while series-A is entirely smectogenic without exhibition of any nemetic character. Moreover smectic thermal stability of series-A is lower than series-1, investigated presently . Nematic thermal stability of series-1 is 139.1 ^oC, while it is zero for series-A. Thus highly polarizable –$COOCH_2$-CH_3 group induces nemetic mesophase if it is laterally substituted which causes steric hindrance and high magnitude of polarizability in case of seris-1. While same –$COOCH_2$-CH_3 terminally situated end group induces only smectic character with absences of nemetic mesophase due to lower polarizability as a consequence of linear shape. Mesogenic range varied from 5.0 ^oC to 44.0 ^oC and series is of middle ordered melting type. Smectic mesophase commences from dodecyl derivative in present series while it commences from fifth member of the series in case of series-A. The cause of such behaviour is attributed to the extent of noncoplanarity caused by molecules of laterally substituted –$COOCH_2$-CH_3 group which is more than the same group substituted linearly as an end group in series-A which is less noncoplanar. In general presently investigated titled homologous series-1 is predominantly nematogenic and partly smectogenic.

CONCLUSION

Ortho substituted –$COOCH_2$-CH_3 functional group is more efficient to induce nematogenic character, while same group linearly linked as end group in para position of central group induced only smectogenic character without exhibition of nematogenic character. This conclusion supports the earlier views [1,7]

Acknowledgement
Authors acknowledge thanks to the Applied chemistry deptt, fac, of Tech. & Engg, M.S. Uni. of Baroda, Vadodara. CSMCRI Bhavnagar and RSIC Lucknow laboratory for their valuable co-operation in the work and analytical services.

REFERENCES

[1] Gray G.W. and Winsor P.A. Liqud crystal and Plastic crystal vol-1,chapter -4,page 103-154 (**1974**), Ellis Harwood Ltd., Chichester John Willey and sons Inc. New York, London, Sydney, Toronto.
[2] Gray G.W. Molecular structure and the properties of Liquid Crystal, Academic Press, London (**1962**)
[3] Dave J.S. and Vora R.A. “Liquid crystal and ordered fluids”, eds. Johnson J.F. and Porter. R. S. Plenum press, New York. (**1970),** P.477
[4] Lohar J.M. and Doshi A.V., *Acta Ciencia Indica* vol. XVIIIC, No. 3, p. 245 (**1992**)
[5] Vora R.A. Unpublished work
[6] Bhoya U.C. and Doshi A. V. J. *Ind. Chem Soc.* Vol. 79, March (**2002**), pp 249-251.
[7] (i) Patel R.B., Chauhan M.L. and Doshi A. V. *Der Pharma Chemica*, (**2010**), Vol-2 (6) pp. 157-164. (ii) Patel R.B. and Doshi A. V. *Der Pharma Chemica*, (**2011**), Vol-3 (1) (i) pp. 72-82. (ii) pp. 328-348, (iii) pp 538-548, (iv) pp 557-568, vol.3 (2) pp 147-155.
[8] Vogel A.I. “Text book of practical organic chemistry”, 5th ed. ELBS and Longmann, London. (**1989**), pp 946. C.A., 32, 66348 and C .A., 36,4486., Ph.D. Thesis of C.G. Joshi submitted to Saurastra Uni. Rajkot, March (**1998**).
[9] Prajapati H. R. and Doshi A.V. *Der Pharma Chemica*, **2011**, 3, 2, 370-375.
[10] Bhoya U.C., Shah R.R. and Doshi A. V. *Der Pharma Chemica*, **2011**, 3,(2), 135-141.
[11] Chauhan B.C., Shah R.R. and Doshi A.V. *Der Pharma Chemica*, **2011**, 3(2), 10-117.
[12] Makwana N.G. and Doshi A.V. *Der Pharma Chemica*, **2011**, 3, ,(2), 433-439.
[13] Doshi A.V. and Patel R.B., Makwana N.G., Travadi J.J., Chauhan M.L., Chauhan B.C. *Mol. Cryst. Liq. Cryst.* in press (**2011**).