

Synthesis and Characterization of a Novel Ester Homologous Series : p(p'-n-Alkoxy Benzoyloxy) β -Phenyl -Ethyl Cinnamates

Pandya Shilpa N.¹, Chauhan M.L.*²

¹Research Scholar, Pacific Academy of Higher Education And Research University, Udaipur, Rajasthan, India

²Chemistry Department Sheth P. T. Arts & Science College, Godhra, Gujarat University, Gujarat, India

ABSTRACT

A novel homologous series p(p'-n-Alkoxy Benzoyloxy) β -Phenyl Ethyl Cinnamates is synthesized and studied with a view to understanding and establishing the effects of molecular structure on mesogenic behavior in a series. The mesogenic property commences from third homologue to the last homologue. The transition temperatures of the series are relatively high, ranging between 152 °C and 225°C. The mesogenic range varies between 8 °C (C₁₆) and 37°C (C₆). The novel ester series is nematogenic without exhibition of any smectogenic property and an average thermal stability of 167.6 °C. The mesogenic behavior of the novel series is compared with structurally similar isomeric/non isomeric other known series.

Keywords : Liquid Crystal, Mesogen, Mesomorphism, Nematic, Smectic

I. INTRODUCTION

Molecular rigidity and flexibility [1-7] are important factors related to intermolecular forces of attractions. Suitable magnitudes of anisotropic forces [8-10] of intermolecular attractions can induce mesogenic characteristics in a molecule. Thus, introduction of proper rigidity by two or more phenyl rings bridged through central groups as well as substitution of suitable lateral or terminal functional groups positioned properly at phenyl ring or rings as flexible molecular part can yield liquid crystal substances [11-17] of desired range of temperature. The present investigation concerns a molecular geometry constructed with three phenyl rings bridged through -COO- and central groups as the rigid core and n-alkoxy (terminal) and -CH=CH-COO-CH₂-CH₂-Ph group as flexible part of a molecule, with a view to understanding and establishing the effect of molecular structure on liquid crystal behavior. [18-20]

II. EXPERIMENTAL

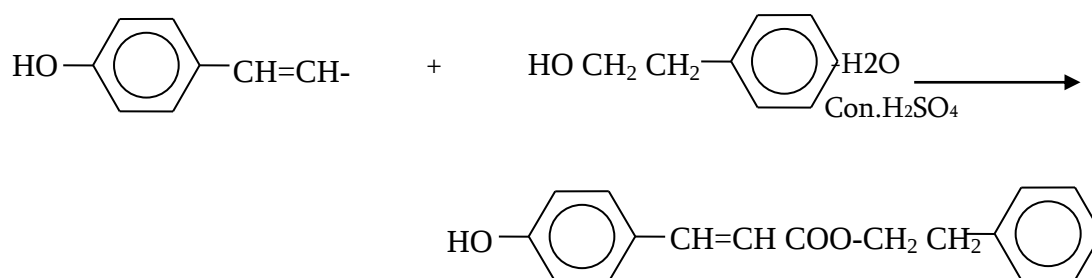
Synthesis Experimental :

- p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor (21), Vora and Dave (22), Vogel (23).
- p - Hydroxy β -phenyl ethyl Cinnamates is prepared by reacting p-hydroxy cinnamic acid with corresponding freshly distilled β -phenyl ethanol in presence of concentrated sulphuric acid mixture.

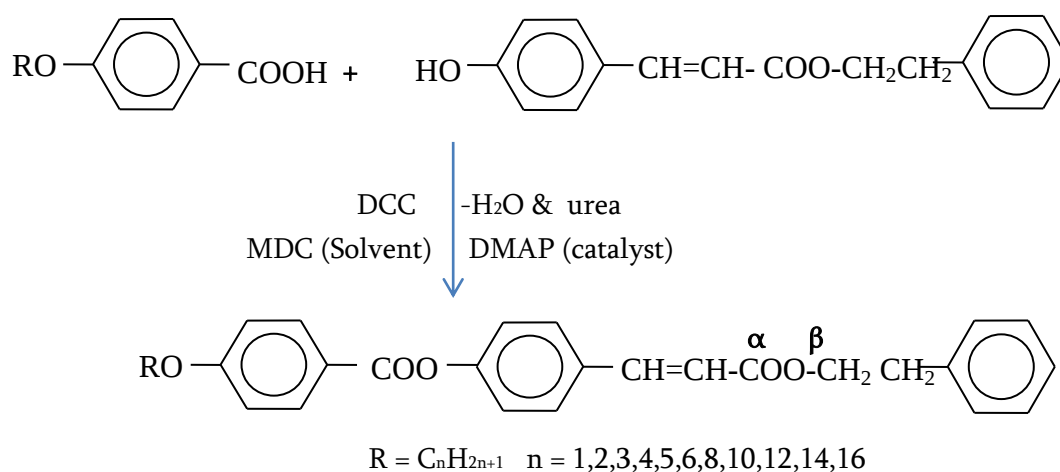
p-n-alkoxy benzoic acids dissolved in MDC with p - Hydroxy β -phenyl ethyl Cinnamates is in portions with DCC & DMAP as catalyst by stirring reaction mixture. (24) Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy cinnamic acid, alkyl halides (R-X), β -phenyl ethanol, KOH, 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) p-Hydroxy β -phenyl ethyl Cinnamates.



(2) p(p'-n-Alkoxy Benzoyloxy) β -Phenyl Ethyl Cinnamates.



Scheme 1. Synthetic route to the series.

Characterization :

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

Sr. No.	Homologue	Molecular Formula	Elements % Found (% Calculated)	
			C	H
1.	Pentyl	C ₂₉ H ₃₀ O ₅	80.60 (79.45)	6.9 (6.8)
2.	Hexyl	C ₃₀ H ₃₂ O ₅	80.25 (79.64)	7.2 (7.0)

Spectral Data :

¹H NMR in ppm : for the Octyloxy derivatives : 1.1, 1.3, 1.5, 1.6, 1.8 (alkyl chain H), 3.8, 3.6, 4.08 (-OCH₂ of -OC₈H₁₇), 7.2, 6.9 (p-di substituted benzene ring and mono substituted benzene ring)

¹H NMR in ppm : for the Decyloxy derivatives: 1.1, 1.3, 1.5, 1.6, 1.8 (alkyl chain H), 3.9, 4.0, 4.06, (-OCH₂ of -OC₁₀H₂₁), 6.8, 7.2, 7.34 (p-di substituted benzene ring and mono substituted benzene ring)

IR in cm⁻¹ : for Hexyloxy derivatives : 895 & 834 cm⁻¹ para di substituted phenyl ring, 1097, 1045, 1245,

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 Dodecyloxy derivatives : 893 & 842 cm⁻¹ para di substituted phenyl ring 1088, 1207, 1261 cm⁻¹ ether linkage, 1452,1600 cm⁻¹ aromatic

ring ,1535,1305 nitro group present,1740 cm⁻¹ ester present, 2866, 2941 long chain alkane present

Texture : by miscibility method;
Threaded nematic C₅
Schlieren nematic - C₈ and C₁₄

Table 1. Transition temperatures in °C

Sr. No.	n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	225
2	Ethyl	-	-	200
3	Propyl	-	198	215
4	Butyl	-	185	198
5	Pentyl	-	162	183
6	Hexyl	-	152	189
7	Octyl	-	156	168
8	Decyl	-	170	198
9	Dodecyl	-	168	183
10	Tetradecyl	-	165	182
11	Hexadecyl	-	152	160

III. RESULTS AND DISCUSSION

p – Hydroxy β-phenyl ethyl Cinnamates. (yield 68 %) is a nonmesomorphic substance. But, on condensing it with dimerized n-alkoxy benzoic acid yielded C₃ to C₁₆ homologues as enantiotropic nematic without exhibition of smectogenic property. The rest of the homologues (C₁ to C₂) are nonmesogenic. Transition temperatures (**Table -1**) 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 rising and 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 than descended as series is ascended up to C₁₂ homologue and then deviated from normal expected behaviors. i.e. it is

rising, instead of 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 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 –CH=CH-COO-CH₂-CH₂-Ph 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. [25-30]The nonmesogenic property of homologues C₁ to C₂ 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 $-\text{CH}=\text{CH}-\text{COO}-\text{CH}_2-\text{CH}_2-\text{Ph}$ terminal situated as end group is high in the nematic order. 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 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. Thus, $-\text{CH}=\text{CH}-\text{COO}-\text{CH}_2-\text{CH}_2-\text{Ph}$ end group present in the molecule of 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 C_1 to C_2 homologues and presence 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 C_1 to C_2 homologue are weakened to such an extent that, even, statically parallel orientation order of molecules C_1 to C_2 is not facilitated to cause nematic mesophase formation. Hence, reasons for nonmesomorphicity character of C_1 to C_2 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 C_{14} and C_{16} 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 $-\text{CH}_2-$ 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** [31] as shown in figure-2.

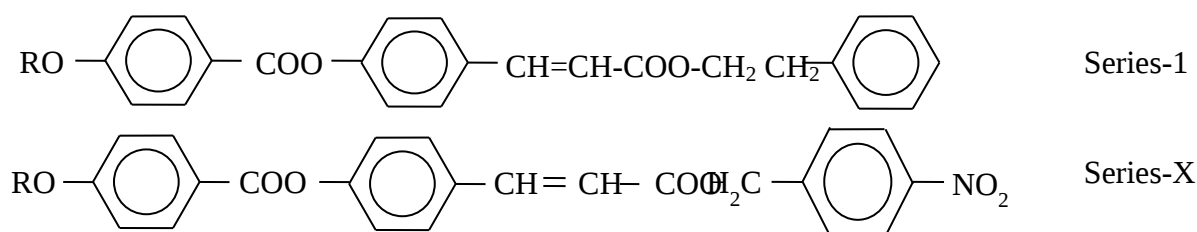


Figure 2. Structurally Similar Series

Table 3. Average thermal stability in °C

Series	1	X
Nematic-Isotropic commencement of nematic phase	167.6 °C. (C ₃ -C ₁₆) C ₃	198.0°C. (C ₆ -C ₁₄) C ₆
Mesophase length range in °C from (Sm+N) C _{nα} to C _{nβ}	8 - 37°C C ₁₆ C ₆	11 - 50°C. C ₆ C ₁₄

From above table-3, it is clear that,

- Presently investigated novel series -1 and X are only nematogenic .
- Nematic mesophase commences from C₃ homologue of series-1 whereas it commences from C₆ 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-CH₂-CH₂-Ph and -CH=CH-COOCH₂-Ph-NO₂. 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 -CH₂-CH₂-Ph for series -1 and CH₂-Ph-NO₂ for series -X respectively. The -CH₂-CH₂-Ph unit of series-1 is longer than -CH₂-Ph-NO₂ group of series -X which links with -Ph-NO₂ common unit of all series under comparison. However linking of uncommon longer unit -COO-CH₂- bonded with common sp² hybridized -C₆H₄ -NO₂ unit . Thus, longer and shorter differing units of present novel series-1 and X bonded with differ tail unit -CH₂-CH₂-Ph and -Ph-NO₂, 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.

IV. 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

- thermal stability
- commencement of mesophase
- total mesophase length for nematic with reference to molecular rigidity/flexibility are as under

Nematic

Rigidity/Flexibility : -CH=CH-COOCH₂-Ph-NO₂>-CH=CH-COO-CH₂-CH₂-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.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

- [1]. F. Reinitzer, *Monatsh* 9. 21 (1888).
- [2]. S. Naemura. *Advance LCD technologies*, *Displays* 22 (1) 2001) P-1.
- [3]. W. S. Kim, S.J.Elston and F.P. Raynes, *Display* 29,(2008), PP. 458-463.
- [4]. Imran Tadwee, Dr. SahanaShahi, VivekRamtekeIftequar Syed, *Liquid crystals pharmaceutical Applications A review*, *IJPRAS*, ISSN 2277-36 vol. 1, Issue 2 (2012), 06-11.
- [5]. E. Hertz B. Lavorel, and o.Faucher, *optical imagine by molecular gas*, *Nature photo* 5 (2011) PP 78-79.
- [6]. G.W. Gray and P.A. Winsor (eds) *Liquid crystals and plastic crystals*. chapter - 6.2 The role of Liquid crystals in life processes by G.T. Stewart vol. 1 pp-308-326.
- [7]. C.A. Calliste, J.C. Le Bail, P.Trouillas, C. PoughA.J.Chulia, L.J.Duroux, *Anticancer, Res.*, 2001, 21, 3949-3956.
- [8]. Y. Jahng L. Zhao, Y Moon, A. Basnet, E. Kim, H.W.Chang, H.K.Ju, T.C Jeong E.S. Lec, *Bioorg. Med. ChemLett.* 2004, 14, 2559-2562.
- [9]. A.Modzelewska, C. Pettit, G.Achanta, N.E. Davidson, P.Huang, S.R.Khan, *Bioorg. Med chem.*, 2006, 14. 3491-3495.
- [10]. G. Rajesh, K. Mansi, K. Srikant, B.Baba sahib, D.Nagesh, S.Kavita, C. Ajay, *chem. pharm. Bull*, 2008, 56, 897-901.
- [11]. Y.S. Lee, S.S.Lim, K.H.Shin, Y.S.Kim, K. Ohuchi, S.H.Jung, *Biol. Pham. Bull*, 2006, 29, 1028-1031.
- [12]. D. Demus, 100 years of Liquid crystal chemist *Mol. Cryst. Liq.cryst* 165 (1988) PP 45-84.
- [13]. D. Demus" Plenary lecture one hundred year of liquid crystal chemistry. *Thermotropic liquid crystals with conventional and unconventional molecular structure" Liq. cryst* 5 (198)
- [14]. C.T. Imrieand G.R. Luckhurst "Liquid cry. dimers and oligomers, in hand book of liquid crystals, law molecular liquid crystals, Vol. 2B, D. Demus, J.W. Goodby, G.W.Graw, H.W. Spiess and V. Villcads. willey VCH, weinhe 1998, pp 801-833.
- [15]. R. A. Vora, A.K. Prajapati, J.B. Kevat and K.K. Raw, *Mesogenic Properties and the effect of 1,2,4,tri substitution on the central benzene nucleus of a three ring Mesogen*. *Liq. Cryst.* 28 (2001) PP 983-998.
- [16]. Doshi et al (i) D.M. suthar and A.V.Doshi, *Mol. Cryst. Liq. Cryst* Vol. 575 pp 76-83 (2013) (ii) H.N. Chauhan and A.V.Doshi, *Mol. Cryst Liq. Cryst* Vol. 570, PP 92-100 (2013) (iii) R.P.Chaudhari, M.L.Chauhan and A.V.Doshi, Vol. 575, pp 88-95 (2013). (iv) U.C.Bhoya ,N.N.Vyas and A.V.Dosi *Mol. Cryst. Liq. Cryst.* Vol. 552, PP 104-110 (2012).
- [17]. YOUNGW R. *Mol. Cryst. Liq. cryst.* Vol. 10, 237 (1970) and DIETRICH, H.J. and STEKIER, E.L. *Mol Cryst. Liq. Cryst.* 16, 263 (1972)
- [18]. D.M. Suthar, A. A. Doshi and A.V.Doshi "study of Liquid crystalline state and evaluation of its Properties through a Novel Homologue series" *Mol. Cryst. Liq. Cryst.* Vol. 582, PP. 79-87, 2013.
- [19]. D.M. Suthar, A.A. Doshi and A.V.Doshi "synthesis and evaluation of a novel Liquid crystalline Homologous series α -4(4'-n alkoxy

- cinnamoyoxy) benzoyl β -3", 4"- Di Methoxy phenyl Ethylenes" Mol. Cryst. Liq. Cryst, Vol. 577; PP 51-58, 2013.
- [20]. G.W. Gray, Molecular structure and properties of liquid crystals, Academic press, London, 1962.
- [21]. G. W. Gray (1974). In; G. W. Gray & P.A. Winsor (eds) Liquid crystals and plastic crystals, chapter - 4 Volume -1 pp 103-153
- [22]. Dave J.S. and Vora R.A. (1970) In J.F.Johnson and R.S. Porter, (Eds.), (Liquid crystals and ordered fluids, plenum Press; New York, P. 477.
- [23]. Vogel. A.I. "Textbook of practical organic chemistry", 5th ed. ELBS and Longmann, London.1989. p946.
- [24]. Brijesh H. Patel and Doshi A.V. Manuscript of a research paper entitled " Synthesis and study of a novel Ester homologous series and evaluation of its liquid crystal behaviour in Relation with Molecular structure"
- [25]. C. T. Imrie, Liq. Crystal dimmers. Struct. Bond 95 (1999) pp 149-192.
- [26]. Hird M., Toyne, K.J. & Gray G.W., Day (1993) Liq. Cryst. 15, 123.
- [27]. Marcos, M. Omenat A., Serrono, J.L. and Ezcurra A. (1992), Adv. Mater, 4. 285.
- [28]. P.J. Collings and M. Hird, Introduction to Liquid crystals chemistry and physics. Teylor and Francis Ltd. U.K. 1998.
- [29]. Hird, M. Toyne, K. J. & Gray G.W. (1993) Liq. Cryst . 14, 741.
- [30]. D.M. Suthar and A.V. Doshi(2013)Mol. Cryst. Liq. Cryst. 571(1).
- [31]. Chauhan M.L., and Patel J.M., Mol. Cryst. Liq. Crystal Journal (Taylor and Francis) with its LCMH 310 dated 14-04-2015

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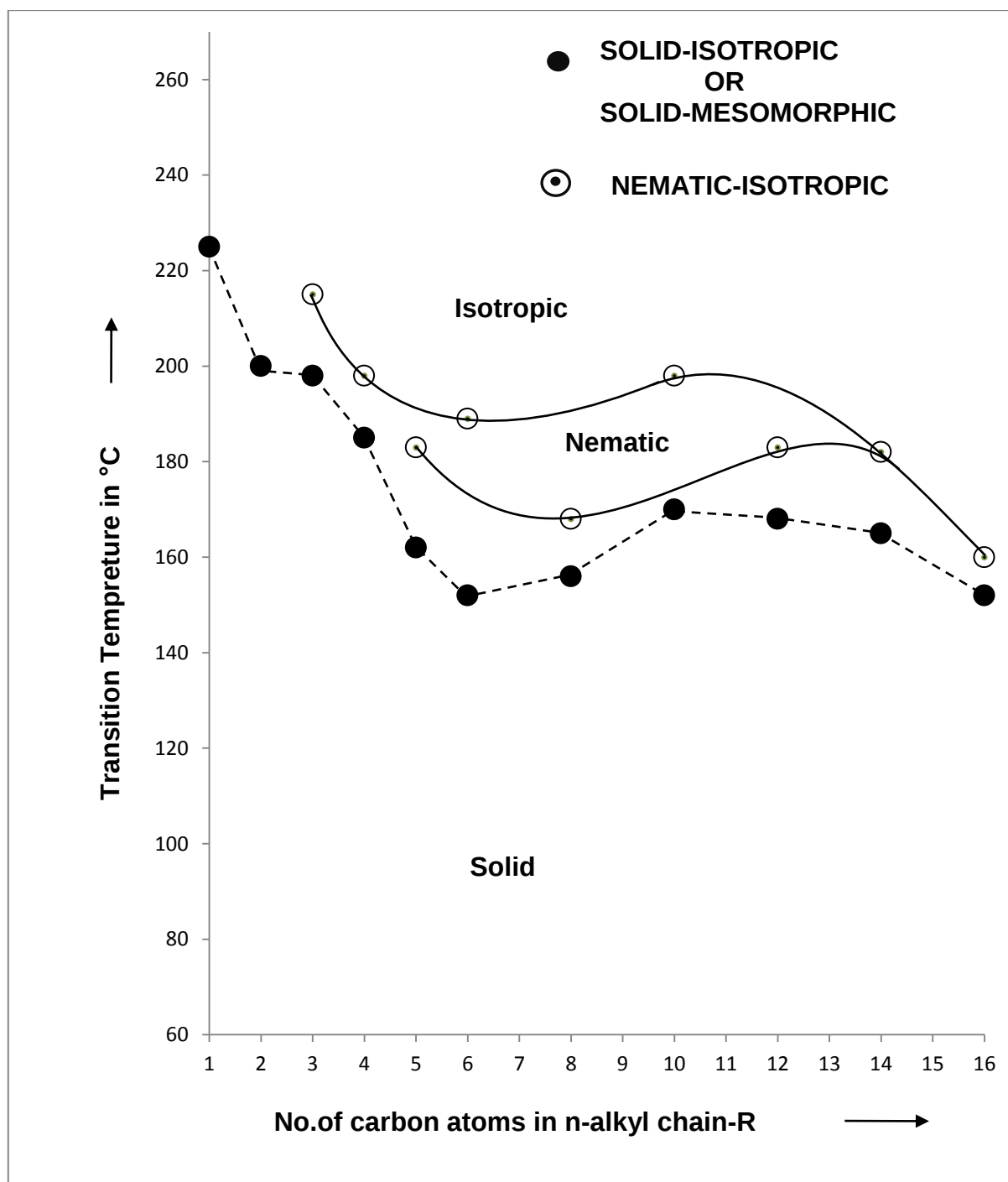
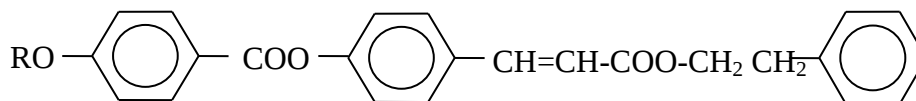


Figure 1. Phase Behavior of Series