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Study of an azoester novel homologous series: 4-[4′-n-alkoxy benzoyloxy]-3-methoxy phenyl azo- 3″- chloro benzenes

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ABSTRACT

Titled homologous series consists of eleven members. Methyl to pentyl and dodecyl to hexadecyl homologues are nonmesomorphic, while; hexyl, octyl and decyl members of the series are mesomorphic. All the three mesomorphic homologues are enantiotropic nematogenic without exhibition of any smectogenic character even in the monotropic condition. Analytical data supports the molecular structures of homologues. Transition temperatures are determined by optical polarizing microscope with heating stage. Mesomorphism exhibited by the series is very poor with short range mesophaselength varying from 24°C to 26°C. Average thermal stability for nematic is 132.6. Thus, series is partly nematogenic with middle ordered melting type. The texture of the nematic mesophase is threaded or schlieren type. Mesomorphic properties of titled series are compared with, structurally similar homologous series.

Keywords: Liquid Crystal; Smectic; Nematic; Mesophase; Mesomorphic

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INTRODUCTION

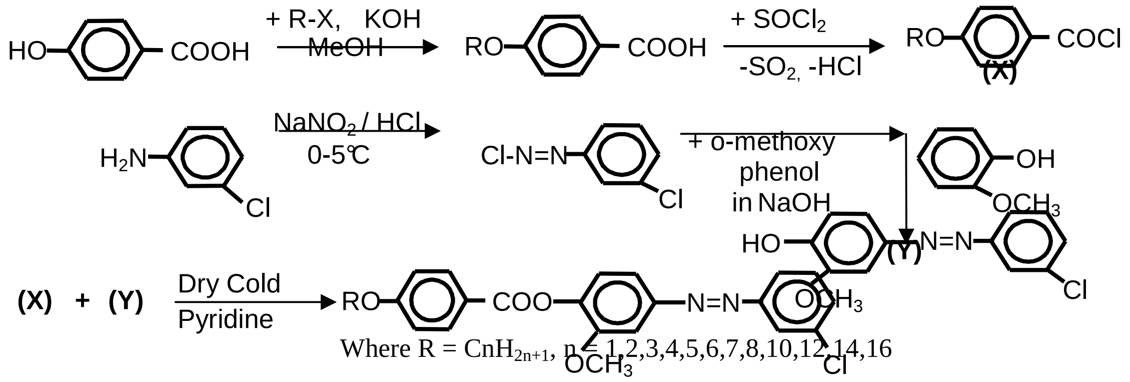
Looking to the industrial utility of liquid crystal (LC) materials in present era, the LC material of varying mesogenic rang was planned to synthesize new LC material through homologous series. Azoester series of LC material is synthesized by modifying molecular moiety through variation in molecular rigidity and flexibility [1,2,3,4]. In present series molecular rigidity is altered by additional linking of central group –N=N- to already ester central group and the molecular flexibility is altered by substituting highly polar -OCH_3 and poorly polar –Cl group at middle and third phenyl rings at meta position to the –N=N- central group respectively. Thus effect of structural variation on LC properties are studied. To which a molecule is broadened and molecular polarizability effect to be observed.

MATERIALS AND METHODS

Characterization:

Some of the selected homologues of the series were characterized by elemental analysis, ^{1}HNMR spectra and IR spectra. C,H,N, Elemental analysis was performed on Perkin Elmer PE 2400 analyzer. ^{1}HNMR spectra were obtained on Bruker spectrometer using $CDCl_3$ as solvent. Texture of the nematogenic homologues were decided by miscibility method. Transition temperatures and liquid crystal properties were investigated by optical polarizing microscopy equipped with heating stage. Thermodynamic quantities enthalpy (ΔH) and entropy (ΔS) are qualitatively discussed instead of DSC scan.

Synthesis:
4-n- alkoxy benzoyl chloride (X) was synthesized from corresponding 4-n-alkoxy benzoic acid using thionyl chloride. 4-n-Alkoxy benzoic acids were prepared from 4-hydroxy benzoic acid using suitable alkylating agent by method of Dave and Vora [5]. 4-Hydroxy 3-methoxy phenyl azo - 3'-chloro benzene (Y) was prepared by known method of Furnis et al. [6]. Final azoesters were prepared by condensing (X) and (Y) in ice cooled pyridine. Product were decomposed, filtered, washed, dried and finally recrystallised till constant melting point obtained. p-Hydroxy benzoic acid, Alkyl halides, Thionyl chloride, Pyridine, KOH, methanol, o-methoxy phenol, m-chloro aniline and other chemicals required for synthesis are used as received. The synthetic route to the series is mentioned below in **Scheme-1.**



Where R = C_nH_{2n+1}, n = 1,2,3,4,5,6,7,8,10,12,14,16

Scheme-1: Synthetic route to the series-1

Table -1 Elemental analysis for the hexyloxy and octyloxy derivatives

	Elemental % found (Compared with % calculated)		
Molecular formula	**C**	**H**	**N**
$C_{26}H_{27}N_2O_4Cl$	66.57 (66.88)	5.82 (5.79)	5.91(6.00)
$C_{28}H_{31}N_2O_4$ Cl	66.91 (67.09)	6.53 (6.27)	5.84 (5.66)

Analytical Data :
NMR: in ppm. Hexyl, 0.911(alkyl group of $–OC_6H_{13}$), 1.805 long $-CH_2-$ chain, 3.915 $–OCH_3$, 3.985 $-OCH_2$, 6.945 & 6.902 & 8.069 & 8.029 (p- sub. Benzene)

Octyl, 0.90 (alkyl group of $–OC_8H_{17}$), 1.32 long $-CH_2-$ chain, 4.05 $-OCH_2$ of ($-O\underline{CH_2}-OC_{12}H_{25}$), 1.83 $-\underline{CH_2}-CH_2-O$, 3.92 $–OCH_3$, 6.919 & 7.004 & 8.148 & 8.192 (p- sub. Benzene)

IR in Cm^{-1}, Hexcyl, V_{max}/cm^{-1} 694 & 771 conforms m-sub. Benzene ring, 831 (p-sub. Benzene rings), 1105, 1197, 1681(–COO- group), 1427(-N=N- group), 1359 & 2850 (alkyl group), 1056(-C-O of ether group), 1028 (Ar-Cl linkage)

Octyl, V_{max}/cm^{-1} 692 & 802 conforms m-sub. Benzene ring, 827 (p-sub. Benzene rings), 1064, 1105 & 1687 (–COO- group), 1419 (-N=N- group), 1031 cm^{-1} (-C-O of ether group), 1028 (Ar-Cl linkage)

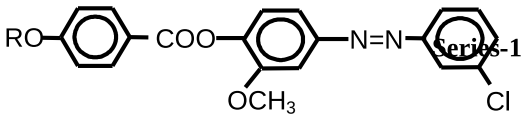
Texture: confirmed by miscibility method
1. Hexyloxy → Nematic threaded
2. Octyloxy → Nematic threaded
3. Decyloxy → Nematic schlieren

RESULTS AND DISCUSSION

Transition temperatures of esters molecules are generally lower than their corresponding n-alkoxy acids on esterification due to disappearance of hydrogen bondings from dimeric acids. Transition temperature may rise or fall of azoester depending upon lateral / terminal and groups substituted to phenyl ring bonded to –N=N- central group. The degree of mesomorphism is also reduced on linking X and Y in pyridine. Presently investigated homologous series consisted of eleven homologues in which hexyl, octyl and decyl derivatives are enantiotropic nematic while the rest of the homologue derivatives are nonmesomorphic. Transition temperatures (table-2) are plotted versus the number of carbon atoms in n-alkyl chain of the left n-alkoxy terminal and related points are joined. A phase diagram for the titled homologous series is obtained as shown in the figure. Solid-isotropic or nematic transition curve follows partly zigzag path of rising and falling and behave in normal manner. Nematic-isotropic transition curve shows descending tendency as series is ascended without showing up of odd-even effect. Smectic mesophase is totally absent. Mesomorphic range is relatively shorter [24°C-26°C].Analytical data support the structures of molecules.

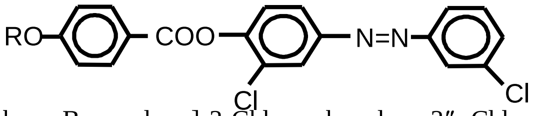
Lowering of transition temperatures of azoester molecules is attributed to the disappearance of hydrogen bonding from dimerised n-alkoxy acids by esterification. Methyl to pentyl and dodecyl to hexadecyl derivatives of the series are unable to withstand the thermal vibrations exposed upon them. Therefore they sharply melt at their melting point without passing through an intermediate state of existence, called liquid crystal state. Nonmesomorphic behavior of homologue may be due to very (zero) short phase length of the homologues concerned or mainly due to the high crystallizing tendency of a sample homologue in which suitable magnitudes of anisotropic forces of attractions as a consequence of its molecular rigidity and flexibility [1,2,3] does not occur. As a result of this, molecules of a sample substance under investigation disalign on the plane of the surface and randomly oriented aimlessly in all possible directions in floating condition without any regularity or ordered molecular arrangement, The observed nematogenic mesophase formation in case of hexyl, octyl and decyl homologue derivative is attributed to the suitable magnitude of intermolecular anisotropic forces of attractions as a consequence of molecular rigidity and flexibility [1,2,3,4] by which molecules are disaligned on the plane of the surface at angle less than 90° and molecules are floating with maintainance of two dimensional array, such that statistically parallel orientational order of molecules is maintained resisting externally applied thermal vibrations within definite range of temperature at constant pressure. Thus, present series is majorly nonmesomorphic and partly nematogenic without exhibition of any smectic character. Broadening of molecules of present series occurs due to laterally substituted methoxy and chloro group at meta position of middle and third phenyl ring respectively with respect to –N=N- central group. Thus, widening of molecules causes two opposing effects [8,9] operating at a time viz (i) widening of a molecule increases intermolecular distance, resulting into reduction of end to end intermolecular anisotropic forces of attractions and, on the other hand at the same time (ii). Broadening of molecule increases the molecular polarizability which enhances intermolecular forces of attractions [8,10,11,12,13,14,15]. But, looking to the mesophase behavior of the series, very few homologues (only three out of eleven) shows nematogenic mesophase formation with absence of smectogenic character. This phase behavior very well support the view to conclude that first (i) effect predominates out of two opposing effects (i) and (ii) i.e. end to end intermolecular anisotropic forces of attractions are weakened to such an extent that, only three homologues molecules could resist exposed thermal vibrations out of eleven homologues to cause mesophase formation with relatively very short phaselength and middle ordered melting behavior.

The mesomorphic or liquid crystal properties viz. mesophaselength, variation in mesomorphic behavior in same series and series to series, commencement of mesophase formation, average thermal stability (table-3) for smectic and/or nematic mesophases; based on molecular polarity and polarizability, length to breadth ratio, aromaticity, geometrical shape and size etc. of presently investigated homologous series (1) is compared with structurally similar homologous series (A) [7b] shown as under in figure-2.



Series-1

4-[4′-n-Alkoxy Benzoyloxy]-3-Methoxy phenyl azo- 3″- Chloro Benzenes.



Series-A

4-[4’-n-Alkoxy Benzoyloxy]-3-Chloro phenylazo-3″- Chloro Benzenes

Where R = C_nH_{2n+1}

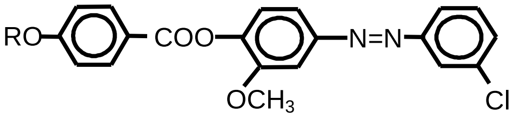
Figure-2: **Structurally similar homologous series**

On comparing the geometrical shape, size, three phenyl rings, left n-alkoxy terminal, central bridges viz. –COO- and –N=N-, laterally substituted –Cl group at the third phenyl ring; series (1) and (A) are identical except laterally substituted $-OCH_3$ and –Cl group at the central phenyl ring identically positioned at meta position to –N=N- central group of series (1) and (A) respectively. Therefore observed variations in mesomorphic properties are attributed to the difference in length to breadth ratio, ratio of molecular polarity to polarizability, steric effect or hindrance caused due to –OCH_3 and –Cl group, intermolecular distance, extent of anisotropic forces of attraction disturbed etc. The average thermal stability and commencement of mesophase are given in table-3 as under.

Table – 2: Transition Temperatures in °C

Compound No	n(for R= -C_nH_{2n+1})	Smectic	Nematic	Isotropic
1	1	---	---	120.0
2	2	---	---	162.0
3	3	---	---	160.0
4	4	---	---	83.0
5	5	---	---	77.0
6	6	---	114.0	140.0
8	8	---	108.0	132.0
9	10	---	101.0	126.0
10	12	---	---	80.0
11	14	---	---	87.0
12	16	---	---	83.0

Series-1: 4- [4'-n-Alkoxy benzoyloxy] 3-Methoxyphenylazo-3''- Chloro benzenes



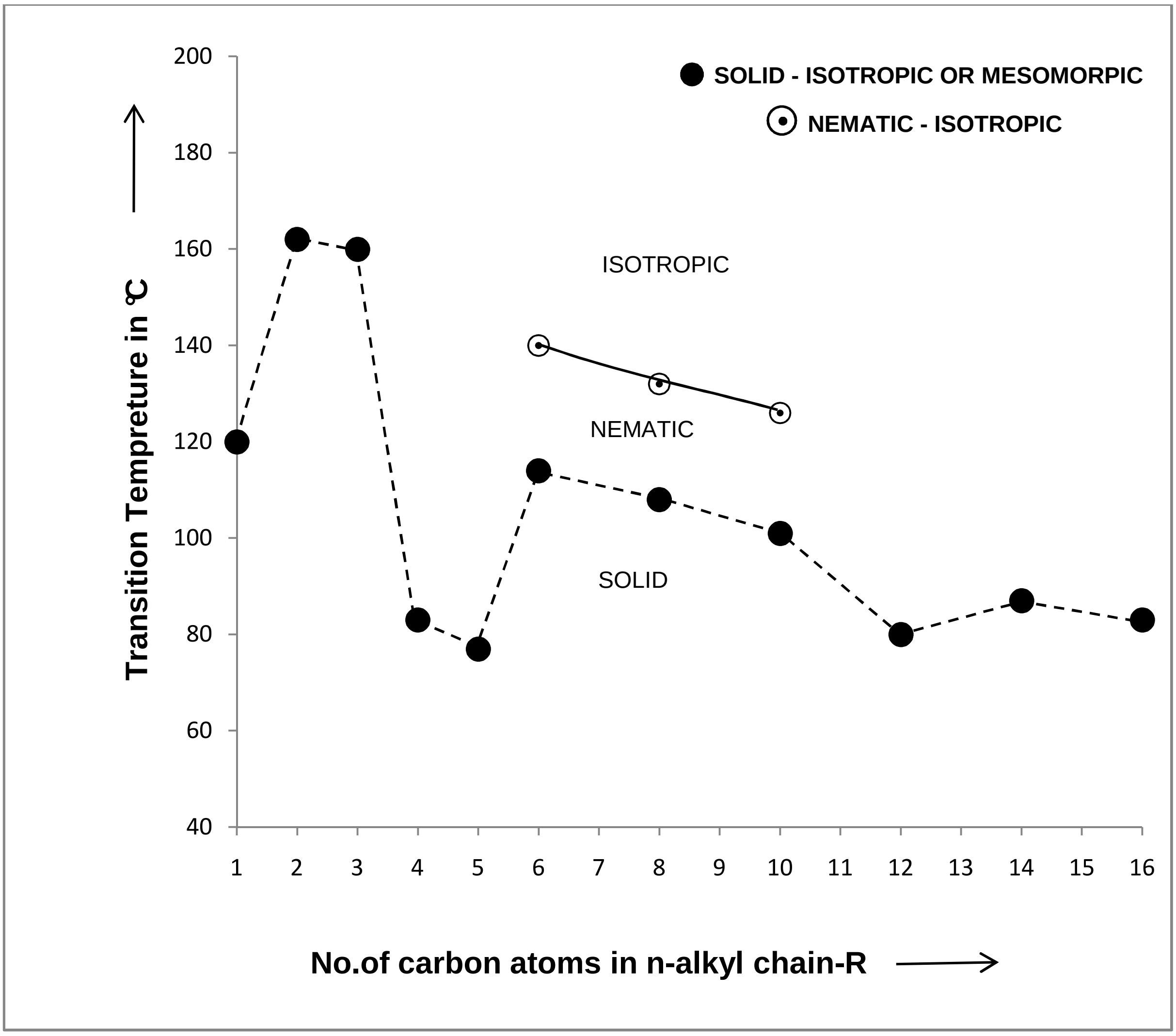


Figure – 2- Phase behavior of a series-4- [4'-n-Alkoxy benzoyloxy] 3-Methoxyphenylazo-3''- Chloro benzenes

Table-3: Average Thermal Stability in °C

Series	1	A
Nematic-isotropic	**132.6** **($C_6 – C_{10}$)**	**130.6** **($C_6 – C_{14}$)**
Commencement of Nematic phase (Nm)	**C_6**	**C_6**

Careful observation of table-3 indicates that, average thermal stability of series (1) is little bit higher than the series (A), because of the highly polar $–OCH_3$ group in comparison with relatively less polar group –Cl. Secondly, commencement of mesophase (only nematic) takes place from sixth homologue of the both series 1 and A. The number of homologues exhibited nematogenic mesophase formation in series (1) is only three viz. hexyl, octyl and decyl homologues derivatives while, number of homologues exhibited nematogenic mesophase are five i.e. hexyl to tetradecyl homologue derivatives of series (A). This difference is attributed to the magnitude of steric hindrance and space occupied by tetrahedraly shaped penta atomic methoxy group and mono atomic chloro group. In this case magnitudes of anisotropic forces of attractions betterly suit to the molecules of series (A) but it does suit little bit less to the molecules of series (1) for higher members of series beyond decyl derivative. Thus, difference of intermolecular distance caused by methoxy group and chloro group affecting molecular polarizability which suits upto tetradecyl derivative of series (A) but, does not favorably suit to the molecules of presently investigated series (1) beyond decyl homologue to form a mesophase in floating condition. Absence of smectogenic character in both the series under comparison is attributed to the misfitting of intermolecular arrangement due to unfit extent of noncoplanarity caused by molecules [7a] of series (1) and (A). Thermal stability of mesophase depends upon heat content or enthalpy change (ΔH) of a molecule concerned at a given temperature. On heating a thermodynamic system (homologue sample) from surroundings, the mesogenic sample homologue resists the thermal variation within definite range of temperatures T_1 and T_2 were entropy $\Delta S = \frac{\Delta H}{T}$ of a sample molecules under investigation vary from ΔS_1 to ΔS_2 during which molecules are floated with two dimensional array but beyond T_2 molecules are randomly oriented in all possible directions and acquire isotropic state. Entropy values become maximum at nematic-isotropic transition temperature. Thus variation in mesogenic properties from homologue to homologue in the same series is attributed to the sequentially added methylene unit at the flexible left n-alkoxy terminal end group, while, the variation in mesogenic properties for the same homologue from series to series is attributed to the varied laterally substituted intact group or groups in present series.

CONCLUSION

(1) Variation in molecular flexibility keeping molecular rigidity constant by laterally substituted group or groups may cause richer or poorer mesomorphism depending upon the magnitudes of predominating effect out of two opposing effects viz. molecular polarizability due to widening of a molecule or intermolecular distance, which are directly related to magnitude of intermolecular cohesion.
(2) Group efficiency order for nematic derived on the basis of average thermal stability is as under

laterally substituted -OCH3 > -Cl group
(3) Variation of mesomorphic properties at constant molecular rigidity from homologue to homologue in the same series is due to the sequencially added methylene unit at the flexible part of a molecule.

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REFERENCES

[1] Marcos, M., Omenat, A., Serrano, J.L., and Ezcurra, A., *Adv. Mater.*, **1992**, 4,285.
[2] Hird, M., Toyne, K.J., and Gray, G.W., Liq. Cryst., **1993,** 14, 741.
[3] Hird, M., Toyne, K.J., Gray, G.W., Day,S.E., & Mc Donnell, D. G., *Liq. Cryst.*, **1993**,15, 123.
[4] Gonzalez, Y., Ros, M. B., Serrano, J.L, and Perezjubind, A., *Liq. Cryst.*, **1998,** 18, 751.
[5] Dave. J. S. and Vora, R. A. ,*Liquid Crystal and Ordered Fluids, Plenum Press: New York.* **1970,** 477.
[6] Furnis, B. S., Hannford, A. J., Smith, P. G. W., and Tatchell, A. R. ,*Vogel's Tex Book of Practical Organic Chemistry, 4th ed., Logman: Sigapore*,**1989.**
[7] (a) Doshi A. V. and Ganatra K.J. ,Proc. *Ind. Acad.Sci. (Chem. Sci.)*, **1999**. 4, 562.
(b) Ph.D. thesisi of D.H.Patel entitled *"Study of mesogenic matter through homologous series and binary mixture"* submitted to Saurashtra university,Rajkot in October **2006**.

[8] Gray, G. and Windsor, P. A., *Liquid Crystal and Plastic Crystals, Ellis Hardwood: Chichester*, **1974.**
[9] Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals, Academic Press; London*, **1962**.
[10] (a) Bhoya, U.C. and Doshi A. V., *J. Indian Chem. Sci*., **2005**, 82, 143.
  (b) Patel V.R. and Doshi A. V., *Der Pharma Chemica*, **2010**, 2, 429.
  (c) Doshi, A. V. and Chauhan, B. C., *Acta Ciencia Indica*, **2003,** 21C, 107.
  (d) Prajapati, H. R. and Doshi, A. V. (2009). I. *Indian Chem. Soc*. **2009**, 86, 470.
  (e) Chauhan, B. C., Shah, R.R., and Doshi, A. V., *Der Pharma Chemica*, **2011**, 3(2), 110-117.
[11] (a) Patel R.B. and Doshi A.V., *Der Pharma Chemica*, **2011**, 3(1), 557-565.
  (b) Bhoya U.C. and Doshi A.V. *Der Pharma Chemica*, **2011**, 3(2), 135-141.
  (c) H.R.Prajapati and Doshi A.V. *Der Pharma Chemica*, **2011**, 3(2), 370-375.
  (d) A.V.Doshi and N.G.Makwana *Der Pharma Chemica*, **2011**, 3(1), 433- 439.
  (e) Chauhan B.C. and Doshi A.V. *Der Pharma Chemica*, **2011**, 3(1), 172-180.
  (f) Joshi C.G.,Patel V.R. and Doshi A.V. *Der Pharma Chemica*, **2011,** 3, 5, 191-197.
  (g) B.C.Chauhan and A.V.Doshi, *Mol.Cryst.Liq.Cryst*., **2012**,Vol. 552: pp. 16-23.
  (h) R.B.Patel, V.R.Patel and A.V.Doshi, *Mol.Cryst.Liq.Cryst*., **2012**,Vol. 552: pp.3-9,
  (i) A.V.Doshi, D.A.Odedara, and R.B.Patel *Mol.Cryst.Liq.Cryst.*, **2012**,Vol. 552: pp. 97-103,
[12] Patel R. B., Chauhan M.L. and Doshi A.V. *Der Pharma Chemica*, **2010,** 2, 6, 157-164
[13] N.G.Makwana and Doshi A.V. *Der Pharma Chemica*, **2011,** 3, 2, 433-439.
[14] Joshi C.G.,Vyas N.N. and Doshi A.V. *Der Pharma Chemica*, **2011,** 3, 5, 233-239.
[15] Bhoya U.C., R.B.Patel and Doshi A.V. *Der Pharma Chemica*, **2011**, 3(3), 115-123.