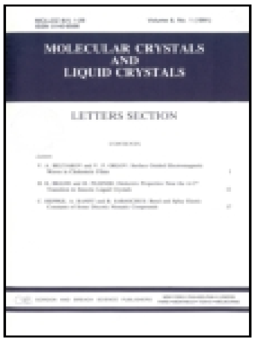

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Mesomorphism dependence on lateral substitution of functional groups and their position in series: 4(4′-*n*-alkoxy benzoyloxy)-3-chloro phenyl azo-2″-methoxy benzenes

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ABSTRACT
Eleven homologues of the title series were synthesized. The methyl-to-pentyl derivatives are nonmesomorphic. The nematic mesophase commences from the sixth member of the series without any smectic phase. An odd–even effect in the nematic–isotropic transition curve is not observed. The nematic mesophase appeared as a threaded or a Schlieren-type texture as observed through a hot-stage polarizing microscope. The nematic–isotropic transition temperatures are between 89°C and 127°C with the mesomorphic range varying from 9°C to 44°C at the hexyl and tetradecyl derivative of the series, respectively. The nematic–isotropic transition curve initially rises and then falls in a normal manner as the series is ascended, but it abnormally rises beyond the 10th homologue. The series is enantiotropic nematic with a middle-ordered melting type. Analytical data support the structures of the molecules. The thermal stability and some other mesomorphic characteristics are compared with structurally similar homologous series. The average nematic–isotropic thermal stability is 105.4°C.

KEYWORDS
Liquid crystal; mesogenic; nematic; polymesomorphism; smectic

Introduction

The increasing utility of liquid crystalline (LC) materials [1–6] inspired the synthesis and evaluation of a novel homologous series. Synthesis of novel LC materials requires the design of a molecular structure that can alter the molecular rigidity and/or flexibility by substituting varying functional as end groups or lateral groups such as –Cl and –OCH_3 at lateral positions of rigid core, which consisted of three phenyl rings and central bridges –COO– and –N=N–, respectively. Thus, molecule is broadened through lateral –Cl and –OCH_3 group to vary molecular rigidity/flexibility [7–11], which may alter intermolecular distance and molecular polarizability and the suitable magnitudes of the anisotropic forces of attractions. Thus, the relation between LC properties and molecular structure can be understood and established [12,13].

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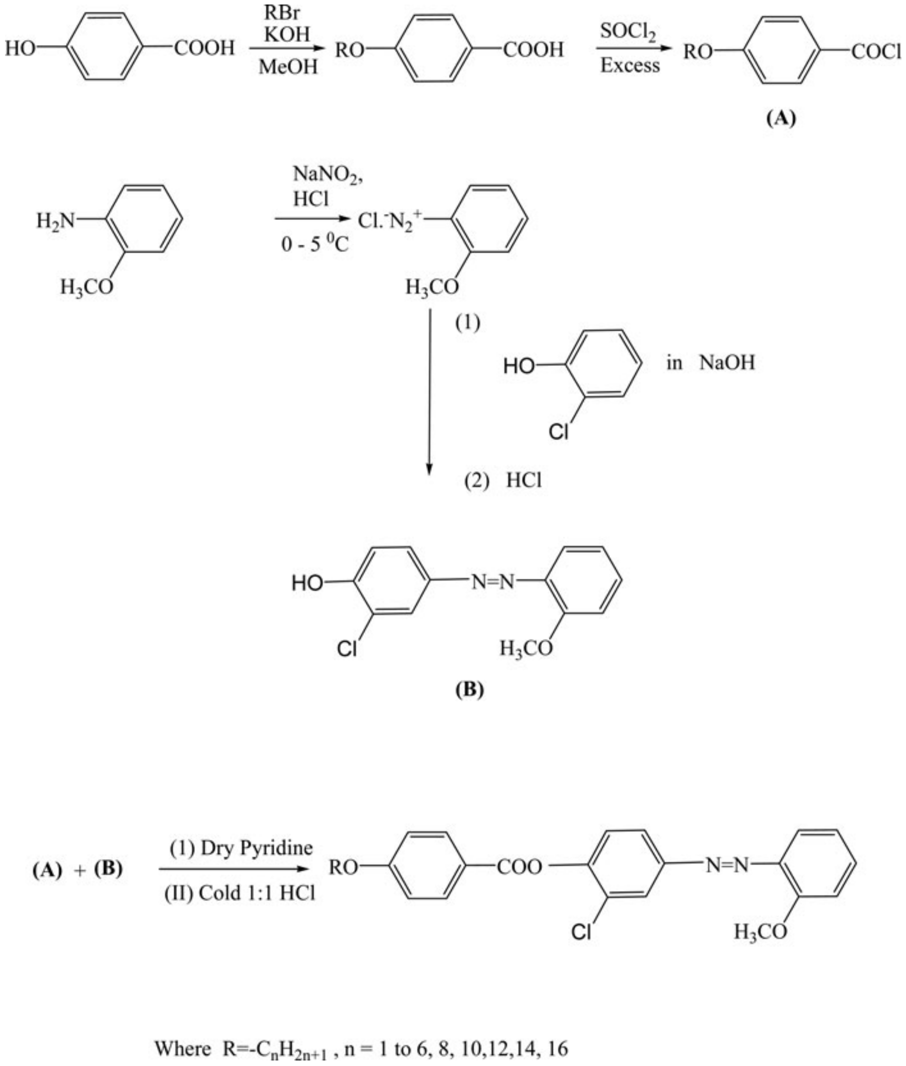
Experimental

Synthesis

3-Chloro -4- hydroxy phenyl azo -2′- methoxy benzene (B) was synthesized by a known method [14]. 4-Hydroxy benzoic acid was alkylated by the corresponding alkylating agents (R-X) and converted to the acid chlorides (A) using $SOCl_2$, by the method of Dave and Vora [15].

4-(4′-n-Alkoxy benzoyloxy)-3-chloro phenyl azo-2″-methoxy benzenes were prepared by condensing (A) and (B) in dry cold pyridine [16]. The novel azoesters were purified in alcohol. The transition temperatures were determined by a hot-stage polarizing microscope. The synthetic route to the series is mentioned in Scheme 1.



Scheme 1. Synthetic route to the series.

Table 1. Elemental analysis for ethoxy, hexyloxy, hexadecyloxy derivatives.

		Elements % found (calculated %)		
Sr. no.	Molecular formula	C	H	N
1	$C_{22}H_{19}N_2O_4Cl$	64.40 (64.31)	4.70 (4.62)	6.80 (6.82)
2	$C_{26}H_{27}N_2O_4Cl$	66.70 (66.88)	5.75 (5.78)	6.08 (6.00)
3	$C_{36}H_{47}N_2O_4Cl$	71.15 (71.22)	7.81 (7.74)	4.55 (4.61)

Characterization

Some selected members of the series were characterized by elemental analysis, Infrared spectra (IR), and ^{1}H NMR spectra. C, H, N composition were determined on Perkin-Elmer PE 2400. ^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ as solvent. IR spectra were recorded on Perkin-Elmer spectrum GX. Textures of the nematic phase were determined by a miscibility method using polarizing microscopy. The data are recorded in Table 1.

Analytical data

IR spectra in cm^{-1} for C_8 and C_{14} homologues

Octyl

2923.9, 2854.0, 1310.5 (alkyl group), 1732, 1164.9 (ester group), 1257.5, 1222.8 (ether group), 1431.1 (–N=N–), 844.8 (*p*-sub. benzene), 752.2 (*o*-sub. benzene), 1060.8 (Ar–Cl linkage).

Tetradecyloxy

2916.2, 2850.6, 1396.4 (alkyl group), 1685.3, 1230.5, 1168.8 (ester group), 1257.5 (ether group), 1431.1 (–N=N–), 844 (*p*-sub. benzene), 756 (*o*-sub. benzene), 1072.3 (Ar–Cl linkage).

^{1}H NMR Spectra in $CDCl_3$ in δ ppm for Octyloxy (C_8) and Decyloxy (C_{10}) Homologues

Octyloxy

0.897 (–CH_3 of –C_8H_{17}), 1.317 (–CH_2 of –C_8H_{17}), 1.829 (–CH_2CH_2O of –C_8H_{17}), 3.654 (–OCH_3), 4.037 (–OCH_2CH_2–), 6.970 and7.014, and 7.062 (*o*-sub. benzene), 7.085 and 7.127 (*o*-sub. benzene), 7.654 and 7.694 (*p*-sub. benzene), 7.897 and 7.940 (*p*-sub. benzene).

Decyl

0.888 (–CH_3 of –$C_{10}H_{21}$), 1.795 (–$COCH_3$), 4.041 (–OCH_2CH_2 of –$C_{10}H_{21}$), 6.905 and 6.971, 7.016 and 7.065 (*p*-sub. benzene), 7.654 and 7.694 (*p*-sub. benzene), 7.887 and 7.941 (*p*-sub. benzene), 1.283 (–CH_2–$C_{10}H_{21}$).

Textures by miscibility method

Nematic

Octyloxy homologue: Threaded texture

Tetradecyloxy homologue: Schlieren texture

Result and discussion

3-Chloro-4-hydroxy phenyl azo-2′-methoxy benzene is a nonliquid crystalline substance. However, linking of phenyl ring through –COO– central bridge and para substituted *n*-alkoxy left terminal group increases the length and aromaticity of the molecule. Increased length and aromaticity increases polarity, polarizability, and length-to-breadth ratio, etc., as a consequence of the net resulted molecular rigidity, and flexibility induces liquid crystallinity. Thus, the added linking units with azo dye, though being nonliquid crystal, produces novel liquid crystal substances except for the first five members and the hexadecyloxy member of the series, which are nonmesomorphic. The mesomorphism exhibited is nematogenic in character and is enantiotropic. The transition temperatures as recorded in Table 1 were plotted versus the number of carbon atoms in *n*-alkyl chain of the left *n*-alkoxy terminal end group, and the phase diagram obtained is shown in Fig. 1.

Solid-isotropic or solid-mesomorphic transition curve follows a zigzag path of falling and rising tendency in normal manner as series is ascended with overall descending tendency. Solid-isotropic transition curve steeply falls from first to sixth member of the series and leveled up rise takes place to the eighth. Then it again falls to the decyl derivative of the series. Solid-isotropic or solid-mesomorphic transition curve again follows the rising path up to tetradecyl member, followed by a fall in its value at hexadecyloxy member with maintenance of a zigzag path. The nematic–isotropic transition curve shows initially rising tendency as the series is ascended with fall at the decyloxy member and then abnormally rises to tetradecyloxy derivative. Thus, methyl-to-pentyl derivatives of the series sharply transformed into isotropic liquid at their melting point relatively at higher temperature because of their short

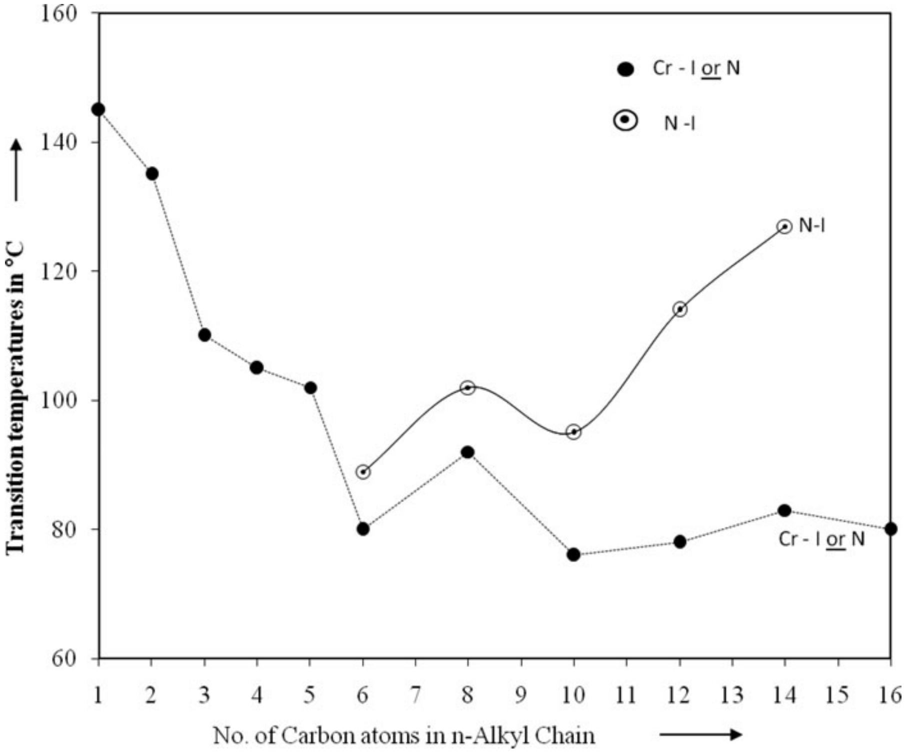


Figure 1. Phase behaviors of series.

Table 2. Transition temperatures of the homologous series: 4(4′-*n*-alkoxy benzoyloxy) -3-chloro phenyl azo-2″-methoxy benzenes.

Compound no.	*n*-alkyl group C_nH_{2n+1} (*n*)	Transition temperatures in °C Smectic (Sm)	 Nematic (N)	 Isotropic (I)
1	C_1	—	—	145.0
2	C_2	—	—	135.0
3	C_3	—	—	110.0
4	C_4	—	—	105.0
5	C_5	—	—	102.0
6	C_6	—	80.0	89.0
7	C_8	—	92.0	102.0
8	C_{10}	—	76.0	95.0
9	C_{12}	—	78.0	114.0
10	C_{14}	—	83.0	127.0
11	C_{16}	—	—	80.0

chain length and higher magnitudes of intermolecular forces of attractions and thermal stability. But in case of hexadecyloxy homologue, the longer *n*-alkyl chain causes the intermolecular attractions to become poorer to resist exposed thermal vibrations. Hence, hexadecyl derivative sharply transformed into isotropic liquid without passing through LC state at relatively lower temperature of melting. Thus, nonmesomorphic groups of methyl-to-pentyl and hexadecyl derivatives are unable to resist thermal vibrations exposed upon them for different reasons and hence melted sharply at their melting point, without showing of LC state. Thus, anti-mesogenic character suggests that neither the parallel orientations of molecules nor two-dimensional sliding layered arrangement of molecules occur in floating condition, by C_1 to C_5 and C_{16} homologue. Absence of odd–even effect in nematic–isotropic transition curve is attributed to the longer *n*-alkyl chain of left *n*-alkoxy terminal end group, which may coil, bend, flex, or couple to lie in major axis of the core, and odd members are absent from and beyond C_6 homologue. The variation of LC properties from homologue to homologue in same series is attributed to the sequentially added methylene unit to the *n*-alkyl chain. Appearance of nematogenic mesophase from hexyl to tetradecyloxy derivative of homologues is due to the disalignment of molecules at an angle less than 90° resisting thermal vibrations exposed upon them within definite range of temperature, during which molecules arrange themselves as statistically parallel orientational two-dimensional order, while floating on the surface. Thus, suitable magnitudes of anisotropic forces of intermolecular end-to-end attractions occur by molecular rigidity and flexibility caused by combined effect of molecular polarity, polarizability, aromaticity, inductive and steric effect, electron–electron interactions, etc.

The molecules from and beyond isotropic temperature are randomly oriented in all possible directions, i.e., high order of molecular disorder or high entropy ($\Delta S = \Delta H/T$) occurs, which, on cooling the same below isotropic temperature, exhibit nematic phase formation in reversible manner.

The nematogenic abnormal phase behavior of the nematic–isotropic transition curve is attributed to the irregularity of the status of longer *n*-alkyl chain of left *n*-alkoxy terminal by its coiling, bending, flexing, or coupling with major axis of core playing role.

The nematic phase appeared has threaded type of texture as determined by miscibility method using hot-stage polarizing microscopy. The mesomorphic properties including average thermal stability (Table 3) and commencement of present homologous series 1 under discussion whose mesomorphic property is compared with other structurally similar known homologous series X [17] and series Y [18] is shown in Fig. 2.

Table 3. Relative thermal stabilities in °C.

	Average thermal stabilities in °C		
Series	Series 1	Series X	Series Y
Smectic-isotropic or smectic-nematic		75.75 (C_{10} to C_{16})	87.55 (C_4 to C_{16})
Commencement of smectic phase		C_{10}	C_4
Nematic-isotropic or isotropic-nematic	105.4 (C_6 to C_{14})	149.4 (C_3 to C_{16})	125.6 (C_3 to C_{16})
Commencement of nematic phase	C_6	C_3	C_3

The homologous series 1, X, and Y contain three phenyl rings, bridged through central –COO– and –N=N– groups and left *n*-alkoxy terminal for the same homologue as common identical features. Series 1 and X differ in their functional groups $-OCH_3$ or –Cl on third phenyl ring at different position of substitution with commonly substituted –Cl group at middle phenyl ring. Series 1 and Y differ in the exchanged substitution –Cl and $-OCH_3$, i.e., isomeric to each other, attached at middle or third phenyl ring irrespective of their position of attachment.

Variations observed for mesogenic properties are directly related to the differing varying features of series 1 from series X and Y. Therefore, degree of mesomorphism and the type or types and the commencement of mesophase formation differ accordingly for the same homologue from series to series under comparison. All the three series, 1, X, and Y, are laterally substituted by either –Cl and/or $-OCH_3$ group. Therefore, molecular broadening due to increased width causes variations in magnitudes of anisotropic forces of intermolecular attractions as

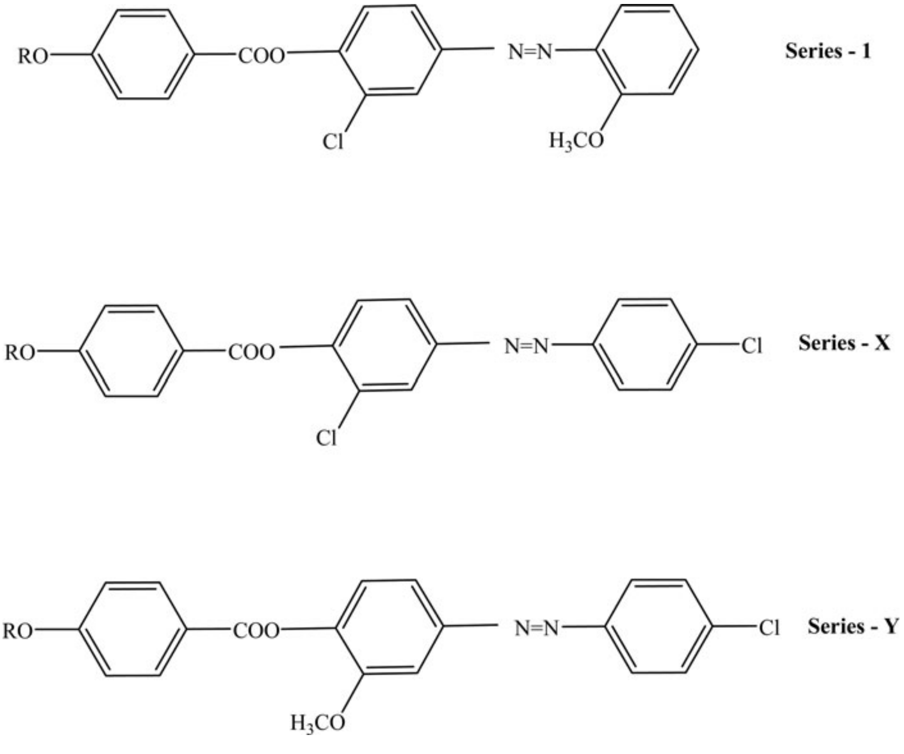


Figure 2. Structurally similar series.

a consequence of molecular rigidity and flexibility, including changing polarizability due to positional difference of lateral group or groups. Molecular broadening causes two opposing effects operating at a time for the same reason: (i) increased molecular width increases intermolecular distance, which reduces intermolecular cohesion; and (ii) broadening of a molecule raises the molecular polarizability, which enhances intermolecular cohesion. The net resulting effect depends upon the predominating effect out of above two opposing effects. Series 1 is only nematogenic, while series X and Y are nematogenic in addition to smectogenic in character, i.e., –Cl group present as right terminal end group increases length-to-breadth ratio, which favorably induces lamellar packing of molecules in the crystal lattices of the molecules of series X and Y due to predominance of (ii) effect related to molecular polarizability effect. The only nematogenic character observed for present series 1 is attributed to the predominance of effect related to weakening of intermolecular adhesion by increased intermolecular distance. The lowest nematic–isotropic thermal stability of series 1 and the absence of its smectic character can be linked to the predominancy of effects. The higher values of nematic–isotropic and smectic–nematic thermal stabilities can be linked to the predominancy of the effect (ii) as discussed above. Early commencement of nematic mesophase (from C_3) by series X and Y as compared to series 1 are also due to factors (i) and (ii), respectively, and the extent of noncoplanarity caused by a respective molecule. Variation in mesogenic properties from series to series for the same homologue is due to varying terminal end group or/and lateral group of fixed polarity.

Conclusions

(1) Mesomorphism and the degree of mesomorphism are very sensitive and susceptible to molecular structure.

(2) Group efficiency order for smectic and nematic derived on the basis of (i) thermal stabilities and (ii) the early commencement of mesophase are as under.

  (i) *Smectic group*: para –Cl and > para-Cl and > meta –Cl and
  efficiency order: meta $-OCH_3$ meta –Cl meta $-OCH_3$
  i.e., (Series-Y) > (Series-X) > (Series-1)
  Nematic Group: (Series-X) > (Series-Y) > (Series-1)

  (ii) *Smectic:* (Series-Y) > (Series-X) > (Series-1)
  Nematic: (Series-X) = (Series-Y) > (Series-1)

(3) Molecular rigidity and flexibility depending upon molecular width and the polarity of substituent operates the magnitudes of anisotropic forces of intermolecular attractions as a result of dipole moment across the long molecular axis, dipole–dipole interactions, dispersion forces, etc.

(4) End-to-end intermolecular attractions are more favored if substituent end group other than –H preferred.

(5) Series is partly mesogenic (nematogenic) and partly nonmesogenic with relatively low thermal stability and mesophase length 9°C to 44°C.

(6) Laterally substituted group may increase or decrease thermal stability and other mesogenic characteristics of LC.

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References

[1] Reinitzer, F. (1888). *Monatsch*, *9*, 421.
[2] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 45.
[3] Demus, D. (1989). *Liq. Cryst.*, *5*, 75.
[4] Naemura, S. (2001). *Displays*, *22*, 1.
[5] Kim, W. S., Elston, S.J., & Raynes, F. P. (2008). *Displays*, *29*, 458.
[6] (a) Doshi *etal.* (i) Suthar, D. M., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *575*, 76. (ii) Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *570*, 92. (iii) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *575*, 88. (iv) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst, Liq. Cryst.*, *552*, 104. (b) Gray, G. W., & Jones, B. (1954). *J. Chem. Soc.*, *2556*.
[7] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc. Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.
[8] Collings, P. J., & Hird, M. (1998). *Introduction to Liquid Crystals: Chemistry and Physics*, Taylor & Francis: London.
[9] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.
[10] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.
[11] Imrie, C. T. (1999). *Liq. Cryst. Dimers. Struct. Bond*, *95*, 149.
[12] Gray, G. W. (1974). In: *Liquid Crystals and Plastic Crystals*, Vol. *624*, Gray, G. W. & Winsor, P. A. (Eds.), pp. 103–153, Ellis Horwood: Chichester.
[13] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.
[14] Furniss, B. S., Hannford, A. J., Smith, P. G. W., & Tatchelll, A. R. (Revisor) (1989). *Vogel's Text Book of Practical Organic Chemistry, 4th ed.*, Longman: Singapore, pp. 563–649.
[15] Dave, J. S., & Vora, R. A. (1970). In: *Liquid Crystal and Ordered Fluids*, Johnson, J. F. & Porter, R. S. (Eds.), p. 477, Plenum Press: New York.
[16] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *577*, 51.
[17] Chauhan, B. C., & Doshi, A. V. (2011). *Der Pharma Chemica*, *3*, 172.
[18] Chauhan, B. C., & Doshi, A. V. (2012). *Der Pharma Chemica*, *3*, 110.