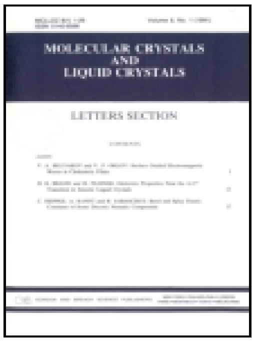

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Mesomorphism in Relation to Molecular Structure with Reference to a Laterally Substituted Homologous Series

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A novel homologous series 4-(4′-n-alkoxy benzoyloxy) 3-methyl phenyl azo-2″, 6″-dimethyl benzenes consists of 12 homologues. The methyl to hexyl derivatives are non-mesomorphic and the rest of the homologues are mesomorphic. Mesomorphism commences from heptyl homologue in a monotropic manner and continues as an enantiotropic nematic for octyl to dodecyl derivatives, and then monotropic mesomorphism as a nematic mesophase reappears for tetradecyl and hexadecyl derivatives without the exhibition of smectogenic character. The textures of the nematic mesophase are threaded, or are schlieren in type. The nematic–isotropic (or vice versa) transition curve of the phase diagram behaves in a normal manner without the exhibition of an odd-even effect. The average thermal stability for nematic to isotropic transition is 126.5°C. Analytical and spectral data confirm the structure of molecules. The mesomorphic to isotropic transition temperatures vary between 56°C and 130°C. The nematogenic mesophase appeared at the lowest temperature of 41.3°C. Transition and melting temperatures are determined using an optical polarizing microscopy equipped with a heating stage. The present novel series is of a low ordered melting type and predominantly nematogenic, without the exhibition of smectogenic character.

Keywords Liquid crystal; mesogen; monotropy; nematic; smectic

Introduction

Our continuous search in the field of liquid crystalline (LC) state has been used in the manufacture of various articles such as electronic display devices, electronic screens, medical instruments [1, 2], pharmaceutical and medicinal preparations, textiles and color industry [3–5], and the study of LCs is important from the point of view novel liquid crystal materials. There are various parts or branches of this field in which engineers, physicists, biologists, and chemists are working in the present era. Our study is restricted or limited to the following.

1. To synthesize novel thermotropic LC substances through low temperature homologous series.

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2. To characterize by elemental analysis and spectral data.
3. To determine thermal data and liquid crystal behavior with a range of liquid crystallinity by an optical polarizing microscopy equipped with a heating stage etc. to understand LC behavior dependence on the molecular structure of a substance.

The proposed homologous series of azo ester molecules consists of three phenyl rings bridged through –COO— and —N=N- central groups playing the role of a rigid core and an n-alkoxy terminal end group playing the role of a flexible core [6–8]. Three methyl groups substituted at lateral positions provide steric hindrance [9] and may reduce transition temperatures, which may be useful for the devices to be operated at the desired temperature. Moreover, the present study is mainly aimed to understand and establish the relation between liquid crystal properties and the molecular structure of a substance.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by the suitable alkylating agent (R-X) by the modified method of Dave and Vora [10]. 2, 6-Dimethyl aniline was diazotized by the usual established method [11, 12] to form an azo dye, 4-hydroxy-3-methyl phenyl azo 2′, 6′-dimethyl benzene (mp 95–97°C). Dimerized 4-n-alkoxy benzoic acid was condensed with the azo dye in dry cold pyridine through corresponding 4-n-alkoxy acid chloride using freshly distilled dry thionyl chloride [13, 14]. The final azo ester derivatives were decomposed, filtered, washed, dried, and crystallized until constant transition temperatures were obtained. 4-Hydroxy benzoic acid, alkyl halides (R-X), thionyle chloride, MeOH, EtOH, KOH, ortho cresol, HCl, 2,6-dimethyl aniline, pyridine were used as received except solvents, which were dried and distilled prior to use.

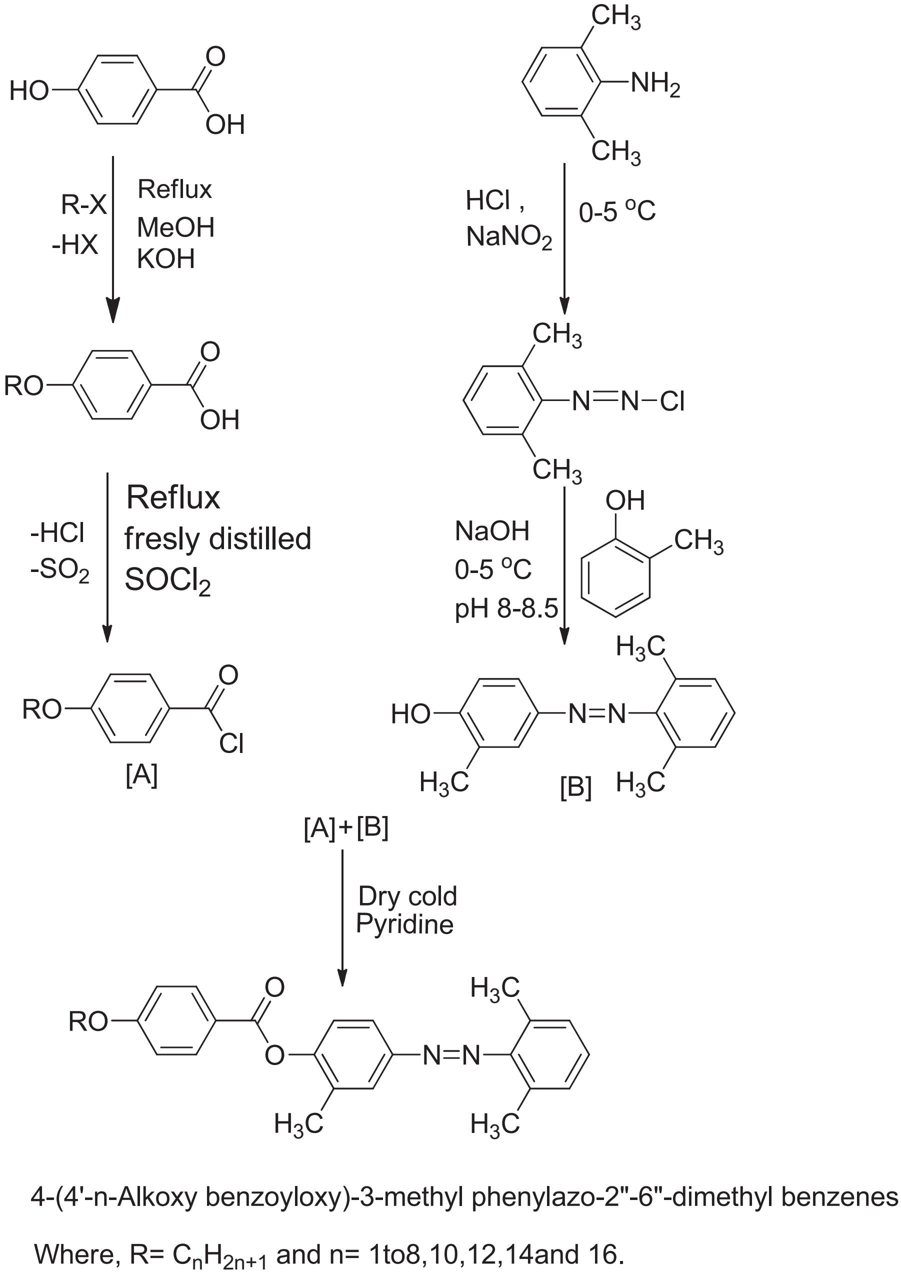
The synthetic route to the series is shown below in Scheme 1.

Characterization

The molecular structures of the novel series were identified using various analytical techniques such as ^{1}H NMR, mass spectroscopy, IR spectroscopy, and elemental analysis. Elemental analysis data obtained from the experimental Euro EA Elemental Analyser (Table 1) and IR data were recorded on a SIMADZU-FTIR-8400 spectrometer. ^{1}H NMR spectra were recorded using BRUKER Avance-III (400 MHz) spectrometer instrument using DMSO-d$_6$ as a solvent. The molecular ion peak obtained from the experimental

Table 1. Elemental analysis for (1) propyloxy, (2) butyloxy, (3) heptyloxy, and (4) octyloxy derivatives

		Elements found (%)			Elements calculated (%)		
Sr. no.	Molecular formula	C	H	N	C	H	N
1.	$C_{25}H_{26}N_2O_3$	74.63	6.53	6.91	74.60	6.51	6.96
2.	$C_{26}H_{26}N_2O_3$	74.92	6.81	6.75	74.97	6.78	6.73
3.	$C_{29}H_{34}N_2O_3$	75.89	7.51	6.13	75.95	7.47	6.11
4.	$C_{30}H_{36}N_2O_3$	76.32	7.64	5.89	76.24	7.68	5.93



Scheme 1. Synthetic route to the series.

EI-MS data was matched with synthesized molecular mass. It was analyzed with the help of SHIMADZU-GC-MS, Model No. QP-2010. All analytical data were matched with the synthesized molecule and found to be satisfied. The liquid crystal behavior and texture types were determined by the miscibility method on microscopic observations.

Spectral Data

NMR in ppm for Decyloxy Derivative. 0.86–0.87(t, 3H, -CH_3 of –$OC_{10}H_{21}$ group), 1.26–1.40 (m, 14H ($-CH_2-)_n$ group), 1.72–1.77 (t, 2H, $-CH_2-CH_2-O-$), 4.08–4.12 (t, 2H, $-CH_2-O-$), 2.306 (s, 9H, CH_3-Ph), 7.13–7.15, 8.11–8.12 (dd, 4H, p-substituted phenyl ring), 7.43–7.45, 7.79–7.88 (m, 3H, o-substituted phenyl ring), 7.77 (m, 3H, 1,6 di-substituted phenyl ring), 7.66–7.67 (d, 1H, in phenyl ring ortho to –N=N-group), 8.02–8.12 (m, 4H, ortho to –COO— and —N=N- group in phenyl ring). The NMR data confirm the molecular structure.

NMR in ppm for Tetradecyloxy Derivative. 0.83–0.85 (t, 3H, -CH_3 of –$OC_{14}H_{29}$ group), 1.24 (m, 22H ($-CH_2-)_n$ group), 1.72–1.77 (q, 2H, $-CH_2-CH_2-O-$), 4.08–4.12 (t, 2H, $-CH_2-O-$), 2.305 (s, 9H, CH_3-Ph), 7.13–7.15, 8.11–8.1 (dd, 4H, p-substituted phenyl ring), 7.43–7.45, 7.79–7.88 (m, 3H, o-substituted phenyl ring), 7.20–7.22, 7.77 (m, 3H, 1,6 disubstituted phenyl ring). The NMR data confirm the molecular structure.

IR in cm^{-1} for Pentyloxy Derivative. 2868, 2949 (C-H Str. of $(-CH_2-)_n$ group of –OC_5H_{11}), 1470, 1593 (aromatic C=C Str.), 3077 (C-H Str. of aromatic ring), 1008, 1166, 1253 (C—O Str. of –COO—group), 1727 (C=O, Str.of –COO- group), 773, 842, 653 (para-, ortho-, and meta-substituted phenyl ring), 1604 (-N=N- Str.). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Dodecyloxy Derivative. 2854, 2924 (C-H Str. of $(-CH_2-)_n$ group of –$OC_{12}H_{25}$), 1465, 1510 (aromatic C=C Str.), 3077 (C-H Str. of aromatic ring), 1012, 1168, 1255 (C-O Str. of –COO-group), 1730 (C=O, Str.of –COO- group), 769, 844, 648 (para-, ortho-, and meta-substituted phenyl ring) 1604 (-N=N- Str.). The IR data are consistent with the molecular structure.

Mass Spectra of Ethoxy Derivative. m/z (rel. int%): 388 $(M)^+$, 245, 205, 121, 93.

Mass spectra of Hexyloxy Derivative. m/z (rel. int%): 444 $(M)^{+,}$ 345, 425, 317, 121.

Result and Discussion

4-Hydroxy 3-methyl phenyl azo 2′, 6′-dimethyl benzene is a non-mesomorphic component of an azoester novel series reported herewith. However, on linking it with dimerized alkoxy acids through their corresponding acid chlorides, azoester homologue derivatives result with lower transition temperature as compared with corresponding n-alkoxy acid. The presently investigated novel homologous series 4-(4′-n-alkoxy benzoyloxy) 3-methyl phenyl azo-2″, 6″-dimethyl benzenes consists of 12 homologues. The methyl to hexyl homologues are non-liquid crystals (NLC) and heptyl to hexadecyl homologue derivatives are liquid crystals (LC). Mesomorphism commences from the heptyl homologue as a monotropic nematic, and mesomorphism from and beyond the octyl homologue to the dodecyl homologue is enantiotropic nematic and finally the tetradecyl and hexadecyl homologues are monotropic nematic. Smectogenic character is totally absent. The transition and melting temperatures (Table 2) as determined by an optical polarizing microscope equipped with a heating stage and plotted against the number of carbon atoms present in an alkyl chain of a left n-alkoxy terminal end group. A phase diagram showing phase behavior of novel series is represented in Fig. 1. Solid mesomorphic/isotropic transition curve adopt a zigzag path of rising and falling values as the series is ascended and finally descended at the hexadecyloxy homologue. The nematic–isotropic transition curve drastically rises from the heptyl to the octyl homologue; descends slowly up to the dodecyl homologue; and then drastically descends to tetradecyl and hexadecyl homologues as series is ascended. Thus, both curves of the phase diagram behave in normal manner. An odd-even effect is

Table 2. Transition temperatures in °C

		Transition temperature in °C		
Compound no.	n-alkyl C_nH_{2n+1} group (n)	Sm	N	Isotropic
1	1	—	—	93.0
2	2	—	—	75.4
3	3	—	—	114.6
4	4	—	—	102.1
5	5	—	—	109.0
6	6	—	—	83.8
7	7	—	(41.3)[a]	70.8
8	8	—	97.2	130.8
9	10	—	93.2	125.7
10	12	—	96.0	123.0
11	14	—	(46.3)[a]	56.0
12	16	—	(48.5)[a]	61.1

Note. [a]Monotropy. Sm = smectic; N = nematic.

absent for the nematic–isotropic (or vice versa) transition curve. Mesomorphic behavior of the novel series from homologue to homologue varies with the addition of methylene units. The mesomorphic range varies from 27.0°C to 33.6°C. Thermal stability for nematic is 126.5°C. Thus, novel series is predominantly nematogenic and partly non-mesogenic whose isotropic temperatures vary between 56°C and 130.8°C. Therefore, the homologous series under discussion is a low melting series.

Mesomorphic properties are induced in a non-mesomorphic azodye molecule by extending molecular length, linking the n-alkoxy acid through acid chloride. An extended molecular length increases the length to breath ratio and lateral to terminal or end-to-end

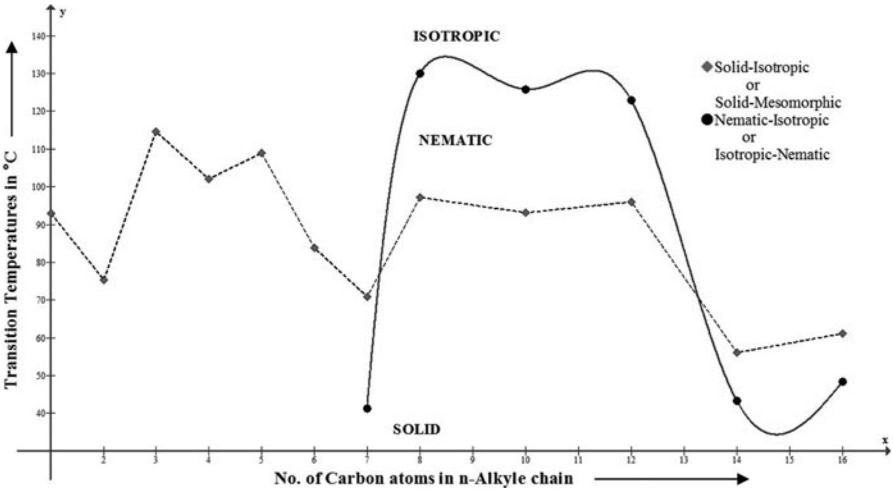


Figure 1. Phase behavior of series.

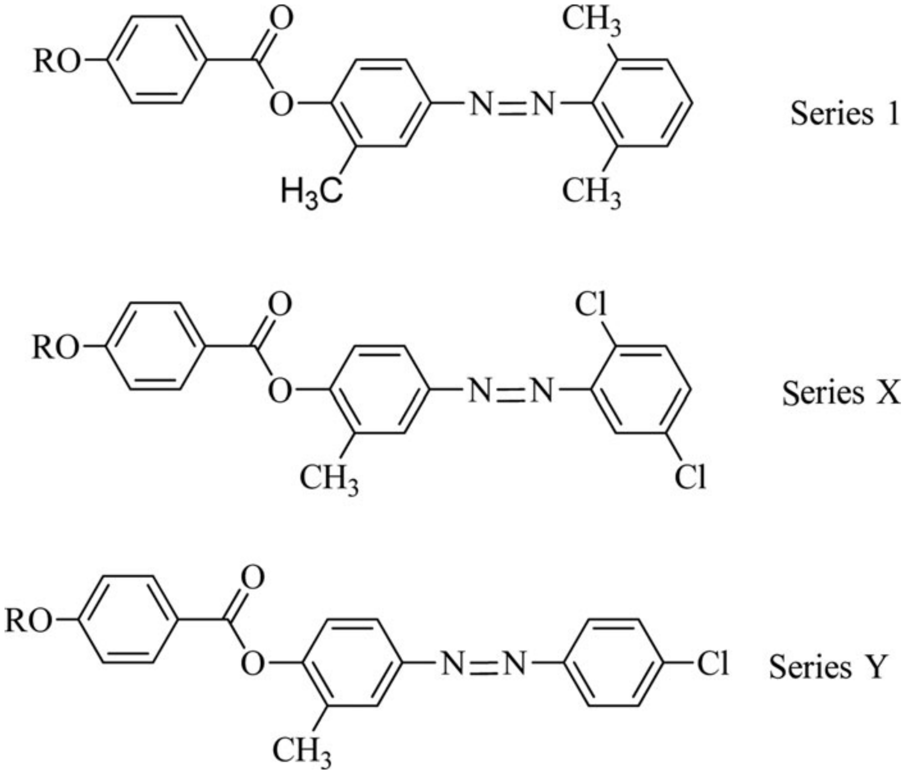


Figure 2. Structurally similar homologous series.

intermolecular anisotropic forces of attraction in suitable magnitudes required to exhibit mesomorphic behavior by heptyl to hexadecyl homologue derivatives as a consequence of favorable molecular rigidity and flexibility [6–8]. Disappearance of dimerisation of n-alkoxy acids and the lowering of transition temperatures of azoester molecules are attributed to the breaking of hydrogen bonding of n-alkoxy acids through the esterification process. The absence of an odd-even effect in the nematic–isotropic transition curve is attributed to the late commencement of mesomorphism from and beyond heptyl homologue. Absence of mesomorphism from methyl to hexyl homologues is due to the high crystallizing tendency, which arises from relatively strong intermolecular forces due to shorter n-alkyl chain. Hence, such molecules under exposed thermal vibrations sharply transform into the isotropic state from the crystalline solid state without passing through a mesomorphic (LC) state. The molecules of the rest of the homologues of the novel series are capable of resisting exposed thermal vibrations reversibly or irreversibly and align with a statistically parallel orientational order of molecules within definite range of temperature. The absence of smectogenic character of the novel series is attributed to the absence of lamellar packing of molecules in their crystal lattices, which is due to the presence of three laterally substituted methyl groups that hinder suitable molecular fitting arrangement to form lamellar molecular packing in their crystal lattices. Vibration in mesomorphic behavior from homologue to homologue in the present novel series is attributed to the sequentially added methylene units, which increase molecular length and lateral to terminal magnitudes of anisotropic forces, including molecular polarity and polarizability affecting intermolecular

Table 3. Average thermal stability in °C

Series →	1	X	Y
Smectic–nematic or smectic–isotropic	—	—	106.6 (C_{12}-C_{16})
Commencement of smectic phase	—	—	C_{10}
Nematic–isotropic	126.5 [C_8-C_{12}]	125.57 [C_6-C_{16}]	161.58 [C_1-C_{16}]
Commencement of nematic phase	C_7	C_6	C_1

adhesion. Thus, suitable magnitudes of intermolecular attractions result in the phenomena of mesomorphism and varying degree and type of mesomorphism. The mesomorphic (LC) behavior of the presently investigated novel series-1 is compared with structurally similar known series X [15] and Y [16] as shown in Fig. 2.

It is clearly seen that homologue series 1, X, and Y are very similar with respect to three phenyl rings bonded through –COO– and –N = N– central bridges and left n-alkoxy (–OR) terminal end group. Therefore, the combined effect of molecular rigidity and flexibility is due to similar molecular parts that operate and contribute equally to mesomorphic behavior. However, variations in mesomorphic behavior in the presently investigated novel series 1 and the homologous series X and Y chosen for comparison have arisen due to the substituted flexible part or functional group or groups of different polarities and the position of substitution which has contributed to the differing magnitudes of anisotropic forces of intermolecular attractions as a consequence of combined and overall effects of molecular rigidity and flexibility. Thus, variations in mesomorphic properties and the degree of mesomorphism from series to series under discussion will vary with the changing part of each series. Table 3 shows the mesomorphic (LC) properties of each series.

Table 3 shows comparative data for series 1, X, and Y as under.

- Homologous series 1 and X are non-smectogenic, while homologous series Y is smectogenic.
- The nematogenic mesophase is exhibited by all homologous series 1, X, and Y under comparison.
- Smectogenic property of series Y commences from the decyloxy homologue, while it does not commence until the last member of series 1 and X.
- Nematogenic mesophase formation commences from the seventh member of series 1, from the sixth member of series X, and from the very first member of series Y.
- The lowest temperatures for the commencement of mesophase formation are 41.3°C, 75.0°C, and 63.0°C for series 1, X, and Y respectively.
- Thermal stability for the nematic of series 1 and X differs by only 1.0 (more) unit or say almost equivalent while it differs (less) by 35.08 units than series Y.

The absence of smectogenic character in series 1 and X and the presence of smectogenic character in series Y are attributed to the absence and presence of lamellar packing of molecules in their respective crystal lattices due to differing extent of non-coplanarity as a consequence of lateral substitutions at two positions of the third phenyl rings of series 1 and X, while homologous series Y possesses only one terminal end group –Cl, which reduces the extent of non-coplanarity as compared with series 1 and X favoring lamellar packing of molecule for series Y to facilitate smectogenic mesophase formation. The resistivity of externally exposed thermal vibrations of series 1, X, and Y is strong enough to maintain statistically parallel orientational order of molecules. However, the suitable magnitudes of anisotropic forces of intermolecular end-to-end attractions differ between the series due to the methyl and chloro group or groups at third phenyl ring of all the series under discussion of comparison, affecting intermolecular closeness, molecular steric hindrance, molecular polarity, and polarizability. Thus, the nematic mesophase commences from the very first member of series Y and from the seventh and sixth member of series 1 and X respectively. The lowest temperatures for the commencement of mesophase either smectic or nematic corresponds for presently investigated series 1. Such behavior may be attributed to the steric hindrance caused by two methyl groups around –N=N– group in 2″ and 6″ positions (ortho to –N=N–). The highest value of thermal stability for the member of a series Y as compared with series 1 and X can be attributed to the differing molecular rigidity and flexibility. Thus, variation in mesomorphic properties from series to series for same homologue is attributed to the changing molecular part of series [17].

Conclusions

1. The group efficiency order derived on the basis of (a) thermal stabilities and (b) the early commencement of mesophase for smectic and nematic are as under:
   (a) Smectic: pera –Cl > 2,5-dichloro = 2,6-dimethyl
   Nematic: pera –Cl > 2, 6-dimethyl > 2, 5-dichloro
   (b) Smectic: pera –Cl > 2, 5-dichloro = 2, 6-dimethyl
   Nematic: pera –Cl > 2, 5-dichloro > 2, 6-dimethyl
2. Presently investigated novel series is nematogenic only of low melting type and a useful range of liquid crystallinity at low temperature.
3. Molecular rigidity and flexibility are very sensitive and susceptible to form liquid crystal mesophase.
4. The variations in mesomorphic properties from homologue to homologue in the same series and for the same homologue from series to series are due to the changing sequentially added methylene unit or units and the changing molecular part of a whole molecule keeping rest of the molecular part intact respectively.
5. The phenomenon of mesomorphism is a direct result of a molecular structure as a consequence of its molecular rigidity and flexibility.

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References

[1] Gray, G. W., & Windsor, P. A. (1974). *Liquid Crystals and Plastic Crystals*, Vol. 1., Chapter 7, Ellis Horwood: Chichester, UK, pp. 327–356.
[2] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.
[3] Kazuki, J. *et al.* (2013). Review. Applications of biomaterials to liquid crystals. *Molecules*, *18*, 4703–4717. doi:10.3390/molecules18044703.

[4] Gray, G. W., & Jones, B. (1954). Mesomorphism and chemical constitution part-III . . . . 4-alkoxy benzoic acid. *J. Chem. Soc.*, 2556–2562.

[5] Demus, D., (1989). Plenary lectures 100 years of liquid crystal chemistry. Thermaotropic liquid crystals with conventional and unconventional molecular structure. *Liq. Cryst., 5*, 75.

[6] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.

[7] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & Mc Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.

[8] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). *Adv. Mater.*, *4*, 285.

[9] Graw, G. W. Ed. (1958). *Steric Effect in Conjugated Systems*. Butterworths: London.

[10] Dave, J. S., & Vora, R. A. (1970). *Liquid Crystal and Ordered Fluids*, J. F. Johonson & R. S. Porter (Eds.), Plenum Press: New York, NY, 477 pp.

[11] Shah, N. H., Vora, R. A., & Jadav, N. D. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 291.

[12] (a) Furniss, B. S., Hannaferd, A. J., Smith, P. W. G., & Tetchell, A. C. (1994). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., Longman: Singapore. (b) Vogel, A. I., & Furniss, B. S. (1994). *Vogel's Textbook of Practical Organic Chemistry*, 4th ed., Longman: Singapore.

[13] Doshi, A. V., & Ganatra, K. J. (1999). *Proc. Ind. Acad. Sci. (Chem.Sci.) 4*(11), 563–568.

[14] Bhoya, U. C., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*(1), 10–15.

[15] Chauhan, B. C., & Doshi, A. V. (2003). *Acta Ciencia Indica Chem.*, *29*(2), 107–112.

[16] Bhoya, U. C., & Doshi, A. V. (2002). *J. Ind. Chem. Soc.*, *79*(3), 249–251.

[17] (a) Patel, V. R., Chuhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, *574*(1), 67–74. (b) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220–227. (c) Chauhan, B. C., Doshi, A. A., & Doshi, A. V. (2005). *Mol. Cryst. Liq. Cryst.*, *574*(1), 67–74. (d) Doshi, A. V., & Ganatra, K. J. (1999). *Mol. Cryst. Liq. Cryst.*, *82*(5), 466–468. (e) Patel, D. H., & Doshi, A. V. (2009). *Mol. Cryst. Liq. Cryst.*, *81*(3), 77–82.