

RESEARCH ARTICLE

SYNTHESIS AND MESOMORPHIC PHASE BEHAVIOR OF TERMINAL BENZO
[1,3] DIOXOLE RING

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ABSTRACT

A new homologous series has been synthesized and studied to explore the impact of adding alkyl chains and a fused heterocyclic ring on mesomorphic properties. The series includes 12 homologues (G_1 - G_{12}), all of which exhibit smectic mesophase. Textural analysis and phase transition temperatures were measured using polarizing optical microscopy with a heating stage. The molecular structures were confirmed using ^1H NMR, FTIR, and mass spectrometry. The incorporation of the 5-amino benzo [1,3] dioxole ring into the molecular structure improved thermal stability, with all derivatives maintaining stability between 48.3°C and 140.4°C. The average thermal stabilities for the smectic was significantly higher than those commonly seen in similar compounds, offering valuable insights for the development of liquid crystalline materials.

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INTRODUCTION

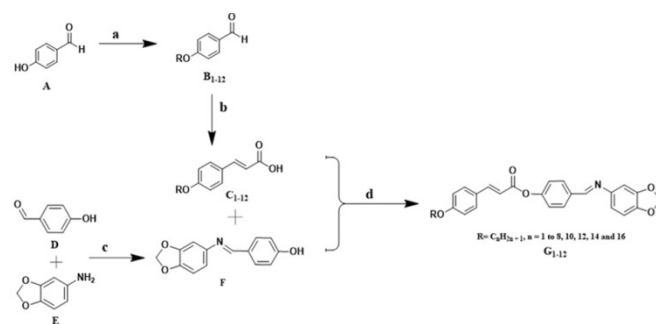
Liquid crystals (LCs) have emerged as a class of materials with exceptional properties that have found applications in various fields, including display technology, optical devices, and sensors (Yang and Wu 2014; Demus *et al.* 2011; Singh 2024). The design and synthesis of new LC materials with tailored properties remain a focal point of research. This study focuses on the synthesis of a new homologous series of LCs incorporating a unique combination of structural features: an linkage of imine and a cinnamoxo and an alkoxy terminal group, all anchored to a fused dioxole ring. The imine functionality, known for its electron-rich character, is expected to enhance polarizability and influence mesophase behavior (Ahmed *et al.* 2019; Hagar, Ahmed, and Saad 2018; Dudhagara *et al.* 2015; Maheta and bhoya 2016). The cinnamoxo linkage, characterized by its rigid rod-like structure, is anticipated to promote liquid crystalline properties (Bhola and Bhoya 2016b; Muniya and Patel 2016; Bhola and Bhoya 2016; Bhola and Bhoya 2016). The alkoxy terminal chain is expected to modulate the mesophase range and transition temperatures (Solanki, Sharma, and Patel 2016; Jain and Patel 2016; Kotadiya and Bhoya 2015). The incorporation of a fused dioxole ring aims to increase molecular rigidity and stability, potentially influencing the overall LC properties (Lin *et al.* 2000; B. Thaker *et al.* 2017). By combining these structural elements, we aim to develop thermal stability of LC materials with potential for advanced applications. This research seeks to establish a synthetic route for these new compounds and to investigate the correlation between molecular structure and mesomorphic properties, providing valuable insights for the rational design of future LC materials.

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EXPERIMENTAL

Synthesis: 4-n-Alkoxy benzaldehyde was synthesized by refluxing 4-hydroxy benzaldehyde (A) (1 equiv.) with n-alkyl bromides (1.5 equiv.) in the presence of potassium carbonate (1.2 equiv.) and DMF as solvent (Dave and Vora 1970) at 60^o-70^oC. The resulting 4-n-alkoxy benzaldehyde (B_{1-12}) (1 equiv.) were reacted with malonic acid (2 equiv.) in the presence of 1-2 drops of piperidine and pyridine as solvent at 60^o-70^oC to yield 4-n-alkoxy cinnamic acid (C_{1-12}) (Kempe *et al.* 2008). 4-Hydroxy benzal-5'-amino benzo [1,3] dioxole (F) was prepared by an established method (Thaker *et al.* 2013). Coupling of compound $C_{(1-12)}$ and F is done by steglich esterification to yield 4-(4'-n-alkoxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole (G_{1-12}) (Neises and Steglich 1978). The synthetic route to the novel homologous series of Schiff's bas cinnamoyl ester derivatives is under mentioned in scheme 1.



a = K_2CO_3 , DMF, R-Br, 60^o-70^oC, 18-20hrs, b = $\text{CH}_2(\text{COOH})_2$, Piperidine, pyridine, 60^o-70^oC, 10-12 hrs, c = acetic acid, MeOH, r.t., 4-6hrs, d = DCC, DMAP, DCM, r.t., 3-4hrs. Where, DMF= Dimethyl formamide, MeOH = Methanol, DCC= N, N'-dicyclohexylcarbodiimide, DMAP= 4-(Dimethylamino) pyridine.

Scheme 1. Synthesis route to the homologous series

Characterization: Some member of series was characterized by elemental analysis (Table 1) on EuroEA Elemental Analyzer. ^1H NMR were recorded on Bruker spectrometer using CDCl_3 solvent (Figure 1 and 2), IR Spectra were recorded on Shimadzu FTIR-8400 (Figure 3 and 4), Mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010 (Figure 5). The thermal behavior recorded on Differential scanning calorimeter (Figure 6 and 7) model no. Shimadzu, shinapore DSC-60 and mesomorphic properties recorder on polarized optical microscopy model no. Nikon Eclipse 400/TU Plan ELWD 20 X/0.40.

Hz, 2H), 6.9295 (d, $J = 9$ Hz, 2H), 6.838 – 6.825 (m, 2H), 6.765 (dd, $J = 6, 2.0$ Hz, 1H), 6.4915 (d, $J = 16.2$ Hz, 1H), 6.00 (s, 2H), 4.005 (t, $J = 6$ Hz, 2H), 1.827 – 1.780 (m, 2H), 1.490-1.440 (m, 2H), 1.385 – 1.255 (m, 6H), 0.893 (t, $J = 4.4$ Hz, 3H).

$^1\text{HNMR}$ in ppm for 4-(4'-decyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3]dioxole G_9

^1H NMR (600 MHz, CDCl_3) δ 8.44 (s, 1H), 7.95 – 7.90 (m, 2H), 7.84 (d, $J = 15.9$ Hz, 1H), 7.53 (d, $J = 6.8$ Hz, 1H), 7.28 (d, $J = 8.5$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.80 – 6.74

Table 1. Elemental analysis for (1) Hexyloxy G_6 (2) Octyloxy G_8 (3) Decyloxy G_9 derivatives

Sr. no	Molecular formula	Element % found				Element % calculated			
		C	H	N	O	C	H	N	O
1	$\text{C}_{29}\text{H}_{29}\text{NO}_5(\text{G}_6)$	73.91	6.18	2.99	16.94	73.87	6.20	2.97	16.96
2	$\text{C}_{31}\text{H}_{33}\text{NO}_5(\text{G}_8)$	74.56	6.64	2.84	16.02	74.53	6.66	2.80	16.01
3	$\text{C}_{33}\text{H}_{37}\text{NO}_5(\text{G}_9)$	75.17	7.05	2.66	15.13	75.12	7.07	2.65	15.16

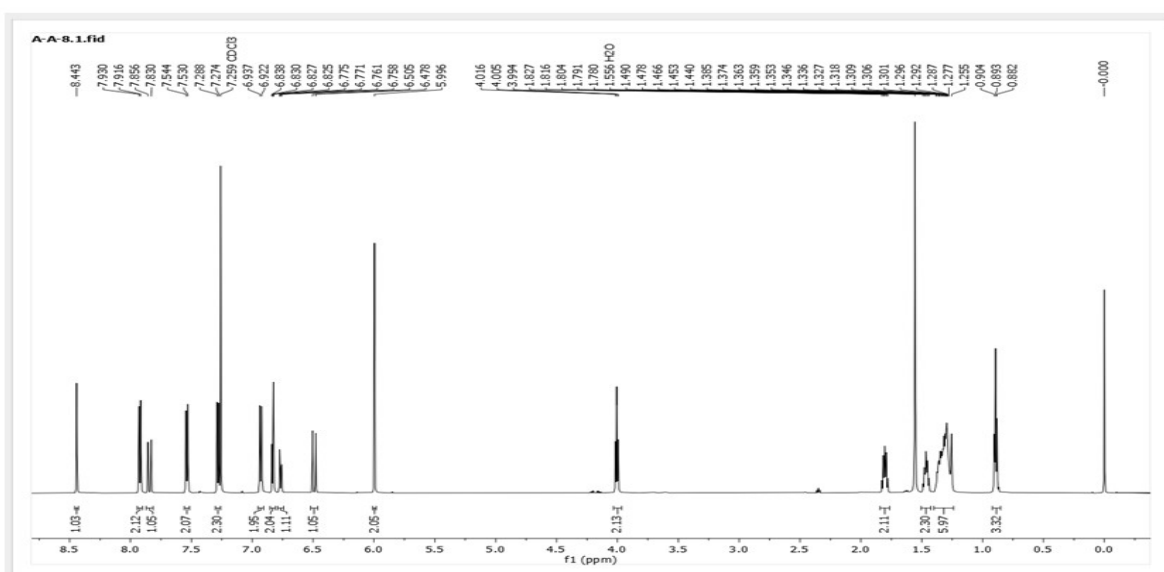


Figure 1. $^1\text{HNMR}$ in ppm for 4-(4'-octyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_8

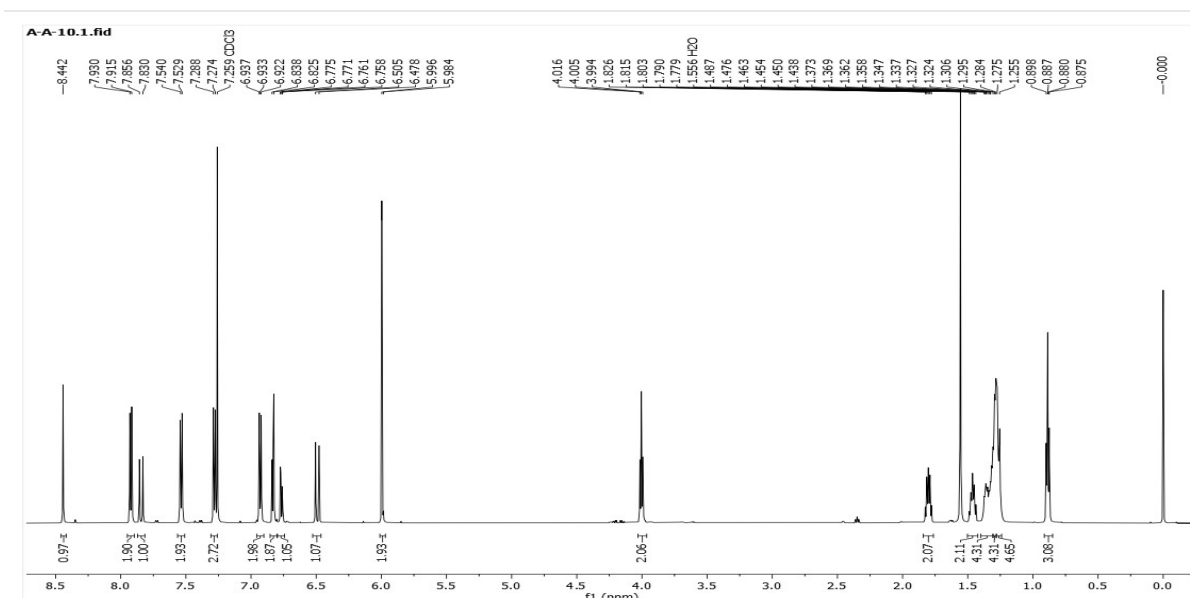


Figure 2. $^1\text{HNMR}$ in ppm for 4-(4'-decyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_9

Analytical data

Spectral data

$^1\text{HNMR}$ in ppm for 4-(4'-octyloxy cinnamoyloxy) benzal 5'' aminobenzo[1,3]dioxole G_8

^1H NMR (600 MHz, CDCl_3) δ 8.443 (s, 1H), 7.925 (d, $J = 6$ Hz, 2H), 7.845 (d, $J = 18$ Hz, 1H), 7.534 (d, $J = 6$ Hz, 2H), 7.281 (d, $J = 8.4$

(m, 1H), 6.49 (d, $J = 15.9$ Hz, 1H), 6.00 (s, 2H), 4.00 (t, $J = 6.5$ Hz, 2H), 1.84 – 1.76 (m, 2H), 1.50 – 1.42 (m, 2H), 1.40 – 1.29 (m, 4H), 1.30 (s, 2H), 1.28 (s, 4H), 1.26 (d, $J = 11.7$ Hz, 4H), 0.89 (t, $J = 6.9$ Hz, 3H).

IR in cm^{-1} for 4-(4'-butyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3]dioxole G_4

IR: (KBr) 3190.37 (C-H stretching of alkene distributed), 2951.19 and 2874.03 (C-H stretching of $-(CH_2)-$ group of alkyl chain), 1732.13 (C=O stretching of α, β unsaturated ester), 1600.97 (-CH=N-stretching), 1496.81 (C-C stretching of aromatic ring), 1134.18 (C-O stretching of ester group), 821.70 (p-disubstituted benzene ring)

IR in cm^{-1} for 4-(4'-hexyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3]dioxole G_6

IR: (KBr) 3190.37 (C-H stretching of alkene distributed), 2939.61 and 2866.22 (C-H stretching of $-(CH_2)-$ group of alkyl chain), 1728.28 (C=O stretching of α, β unsaturated ester), 1604.83 (-CH=N-stretching), 1492.95 (C-C stretching of aromatic ring), 1118.75 (C-O stretching of ester group), 821.70 (p-disubstituted benzene ring)

Mass Spectra of 4-(4'-octyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_8

m/z (rel. int%): 499.2, 259.2, 241.0, 147.05, 119.05.

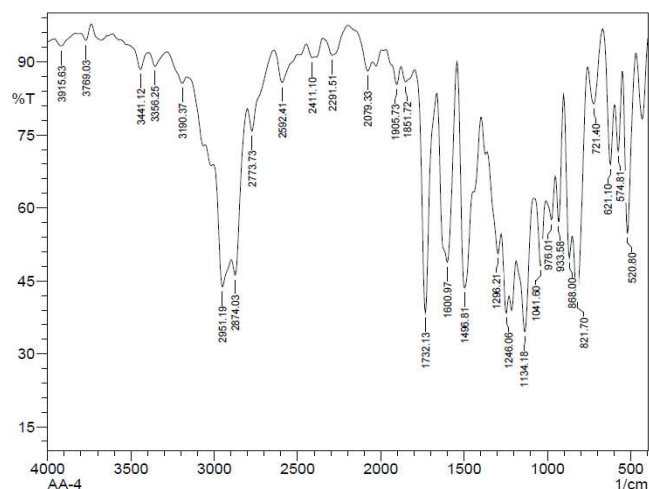


Figure 3. IR in cm^{-1} for 4-(4'-butyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_4

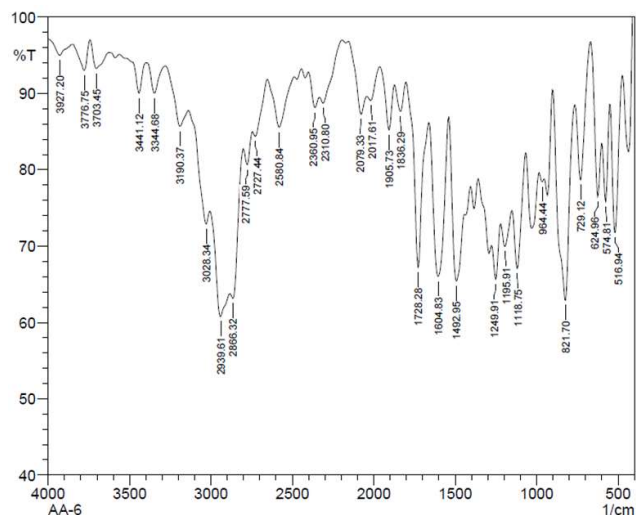


Figure 4. IR in cm^{-1} for 4-(4'-hexyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_6

RESULT AND DISCUSSION

A homologous series of new Schiff's base cinnamoyl ester derived from trans *n*-alkoxycinnamic acid and 4-hydroxy benzal-5''-amino [1,3] dioxole is thermotropically liquid crystalline in nature, it consists of 12 members of series $G_1 - G_{12}$. Mesomorphism commences from G_1 homologue. G_1 to G_{12} homologues are enantiotropically only

smectogenic in nature. Transition temperatures (Table 2) as determined by polarizing optical microscopy are plotted against the number of carbon atoms present in *n*-alkyl chain of left *n*-alkoxy end group (Figure 8), a phase diagram is obtained which consisted of Cr-Sm, Sm-I or vice versa transition curves, showing phase behaviors of series by linking like or related points. Sm-I transition curves exhibited odd-even effect.

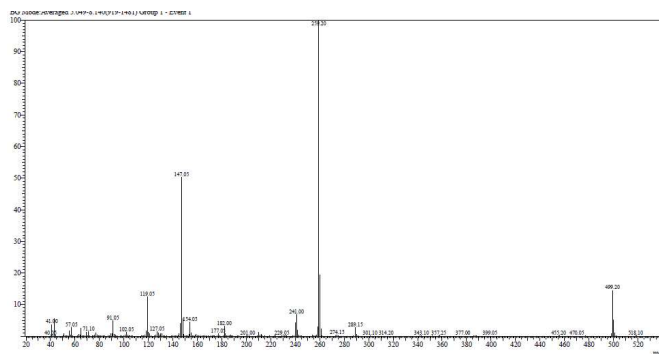


Figure 5. Mass Spectra of 4-(4'-octyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3]dioxole G_8

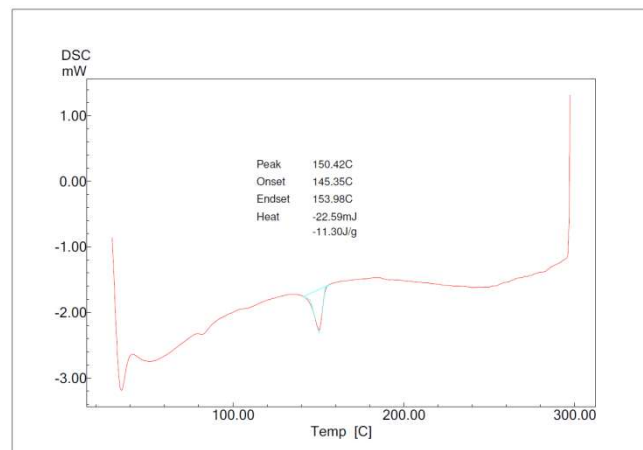


Figure 6. DSC thermogram of 4-(4'-ethyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_2

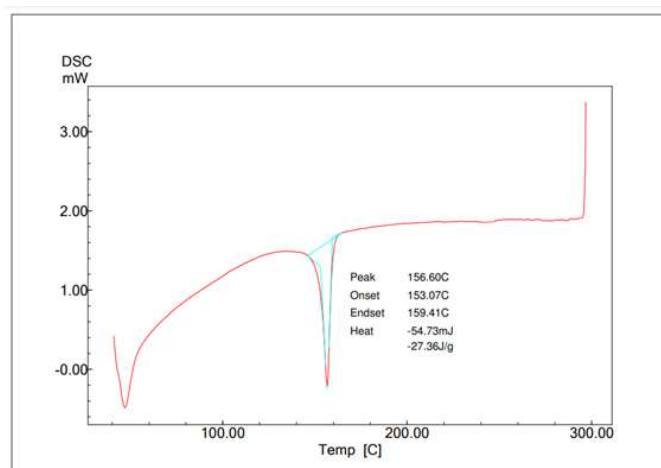


Figure 7. DSC thermogram of 4-(4'-hexyloxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G_6

The Sm-I transition curve for odd members occupy lower positions as compared to even members of a series merge into each other at G_8 homologue. Then, curve prolong as a single curve transition for higher homologue of longer *n*-alkyl chain. However, Cr-Sm transition curves follow a zigzag path of rising and falling with overall flat tendency. Thus, all the transition curves of a phase diagram behaved in normal manner. The mesogenic properties

undergo variations from homologue to homologue in the same new series depending upon member of carbon atoms present in *n*-alkyl chain (-OR) or left terminal end group.

Table 2. Transition temperature in °C

Compound No.	R= <i>n</i> -alkyl chain C _n H _{2n+1}	Transition temperatures in °C		
		Sm	N	Isotropic
G ₁	1	152.8	-	292.5
G ₂	2	153.3	-	283.2
G ₃	3	138.8	-	257.1
G ₄	4	125.3	-	265.7
G ₅	5	116.0	-	225.3
G ₆	6	157.9	-	245.8
G ₇	7	123.6	-	227.2
G ₈	8	125.0	-	227.7
G ₉	10	128.8	-	216.5
G ₁₀	12	101.6	-	200.7
G ₁₁	14	112.1	-	199.3
G ₁₂	16	112.8	-	161.1

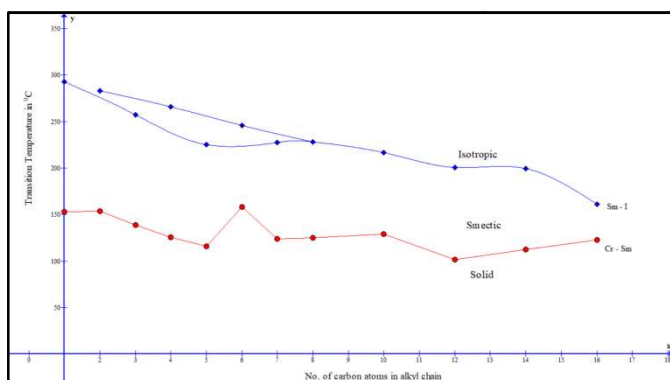


Figure 8. Phase behavior series

An increase in molecular length results in an increase in the molecular length-to-breadth ratio, leading to increased molecular rigidity and reduced flexibility. This elongation also enhances the permanent dipole moment along the long molecular axis, thereby increasing molecular polarity and polarizability. Consequently, intermolecular dispersion and cohesive forces, including proximity effects, are strengthened, which causes favourable and suitable magnitudes of anisotropic forces of cohesion and closeness, which includes smectic or/and nematic mesophases either enantiotropic condition to stabilize suitable mesophase or mesophases within definite ranges of temperature for homologues. All homologues are floating on the surface under exposed thermal vibrations maintain molecular arrangement as required by formation of smectic phase. The exhibition of odd-even effect is attributed to the number of odd and even number of methylene unit or units present in *n*-alkyl chain of left *n*-alkoxy (-OR) group.

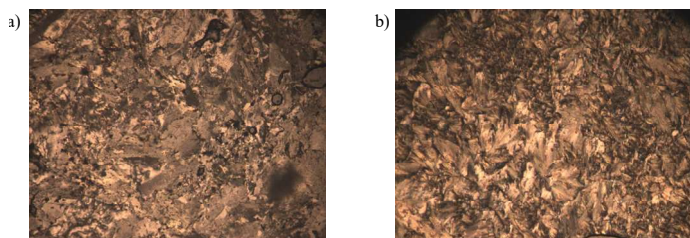


Figure 9. Smectic phase of a) POM Image of 4-(4'-ethoxy cinnamoyloxy) benzal 5'' aminobenzo [1,3] dioxole G₂ and b) POM Image of 4-(4'-dodecyloxy cinnamoyloxy) benzal 5'' aminobenzo[1,3] dioxole G₁₀

The disappearance of odd-even effect from and beyond merging of curves for odd and even numbered homologues is attributed to the unexpected status of longer *n*-alkyl chains by coiling or bending or flexing or coupling with the major axis of a core structure of

molecules, to prolong as a single transition curve. The mesogenic behaviors of presently investigated new series-I are compared with the structurally similar known series-X (Bhola and Bhoya 2016) as shown in Figure 10.

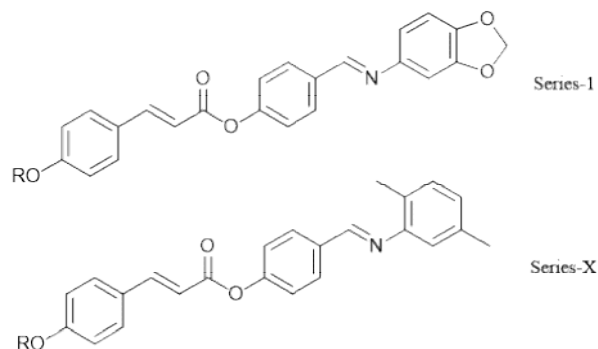


Figure 10. Structurally similar series

Homologous series G and series X selected for comparative study are identical with respect to two phenyl rings, two central bridges -CH=CH-COO- and -CH=N- and left *n*-alkoxy (-OR) group for the same homologue from series to series. But they differ from each other with respect to units of tailed parts i.e. -C₆H₃-O₂-CH₂ and -C₆H₃-(CH₃)₂ of series G and a series X respectively, series G have fused 1,3-dioxalane ring where series X have benzene ring, affecting molecular flexibility for the same homologue. Hence, variations in mesomorphic properties and mesomorphic behaviors can vary with the changing features and their magnitudes of molecular rigidity and flexibility for same homologue from series to series and from homologue to homologue in the same series. Table 3 represents some thermometric properties of series G and X, in comparative manner.

Table 3. Relative thermal stability in °C

Series	G	X
Smectic – Isotropic or Smectic-Nematic	233.5 G ₁ -G ₁₆	100.1 C ₈ -C ₁₈
Commencement of Smectic mesophase	G ₁	C ₆
Nematic-Isotropic	-	110.8 C ₅ -C ₁₀
Commencement of nematic phase	-	C ₂
Total mesophase length range (Sm + N)	48.3(G ₁₆) to 140.4(G ₄)	4.0(C ₁₈) to 41.0(C ₁₂)

From Table 3 indicates that,

- Series-G only shows smectic phases, while series-X exhibits both smectic and nematic phases.
- Smectogenic thermal stability of present series-G is higher than series-X under comparison.
- Smectogenic character commences from G₁ member of series G while G₆ of series X.
- Smectogenic mesophase length stabilities and ranges from 48.3°C to 140.4°C and 4°C and 37°C in series G and series X respectively.
- Total upper and lower mesophase length ranges for series G is relatively higher than series X.

The molecular structures including central bridges and number of phenyl rings for the same homologue, contributing to molecular rigidity are same but, molecular flexibility induced by fused [1,3] dioxole ring of series-G and two -CH₃ (Ortho and meta) group of series X whose polarities and polarizability differed to induce liquid crystalline state on differing suitable magnitudes of anisotropic forces of intermolecular attractions. Fused [1,3] dioxole ring increase molecular rigidity which increase transition temperatures, resulting into increase of thermal stability of present series-G. Whereas, ortho para substituted -CH₃ tail group does not maintain linearity of the molecule, which lowers intermolecular cohesion and proximity. Therefore, transition temperatures and resistivity towards exposed

thermal vibrations and decreased more for the same homologue from series-1 to series X.

Smectic mesophases commences earlier in Series G(G_1) than Series-X(C_6) and nematic mesophase commences Series X(C_2) because, the extent of molecular noncoplanarity vary from series to series for the same homologue due to differing magnitudes of molecular flexibility.

CONCLUSION

- A new Schiff's base cinnamoyl ester homologous series of 12 members (G_1 - G_{12}) are synthesized to understand the effect of fused heterocyclic tail on mesomorphism. The incorporation of the benzo [1,3] dioxole ring into the liquid crystal structures has resulted in enhanced thermal stability across all derivatives, with the presence of smectic mesophase.
- These properties make this moiety particularly promising for applications that operate within the temperature range of 100 to 158°C.
- The group efficiency order derived for smectic on the basis of
 - 1) Thermal stability
Smectic: Series-G > Series-X
 - 2) Commencement of mesophase
Smectic: Series-G > Series-X
 - 3) The total mesophase length ($S_m + N$)
Upper and lower:
Series-G > Series-X
- The findings from this study contribute valuable insights to the design and development of liquid crystalline materials suited for high-temperature environments, offering potential advancements in fields such as display technology and optoelectronics.
- Further investigation into structural modifications and their effects could pave the way for the development of more efficient and tunable liquid crystalline materials.

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