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Mesomorphism dependence of a terminal or lateral alkoxy group

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ABSTRACT

A novel homologous series of thermotropic mesomorphs has been synthesized and studied with a view to understanding and establishing the effect of molecular structure on mesomorphic properties with reference to rigidity and flexibility of the homologues series: $\text{RO-C}_6\text{H}_4\text{-CH=CH-CO-C}_6\text{H}_4\text{-OC}_{18}\text{H}_{37}(\text{n})$. The novel homologous series comprises 13 novel homologues (C_1 to C_{18}), from which 11 homologues are enantiotropically mesogenic (C_3 to C_{18}). Smectogenic mesophase commences from C_7 homologue, and nematogenic mesophase is exhibited by C_3 to C_{18} homologues in enantiotropic manner. Thus, C_7 to C_{18} homologues are enantiotropically smectogenic plus nematogenic. Textures of smectic phase are of the type A or C, and that of nematic phase are threaded or Schlieren as confirmed through an optical polarizing microscope equipped with a heating stage. Transition curve of a phase diagram behaved in a normal manner except N-I transition curve, which shows minor deviating trend (C_{12} to C_{18}) from expected normal behavior. An odd-even effect is exhibited by N-I and Sm-N transition curves. Analytical, spectral, and thermal data confirm the molecular structures of novel homologues. Thermal stabilities for smectic and nematic are 52.7°C and 66.6°C , respectively, whose total mesophase lengths range from 12.0°C to 28.0°C . Thus, novel series of chalcones is a low melting series whose mesogenic transition temperatures vary between 38.0 and 86.0°C .

KEYWORDS

Chalconyl derivative; liquid crystal; nematic enantiotropy; smectic

1. Introduction

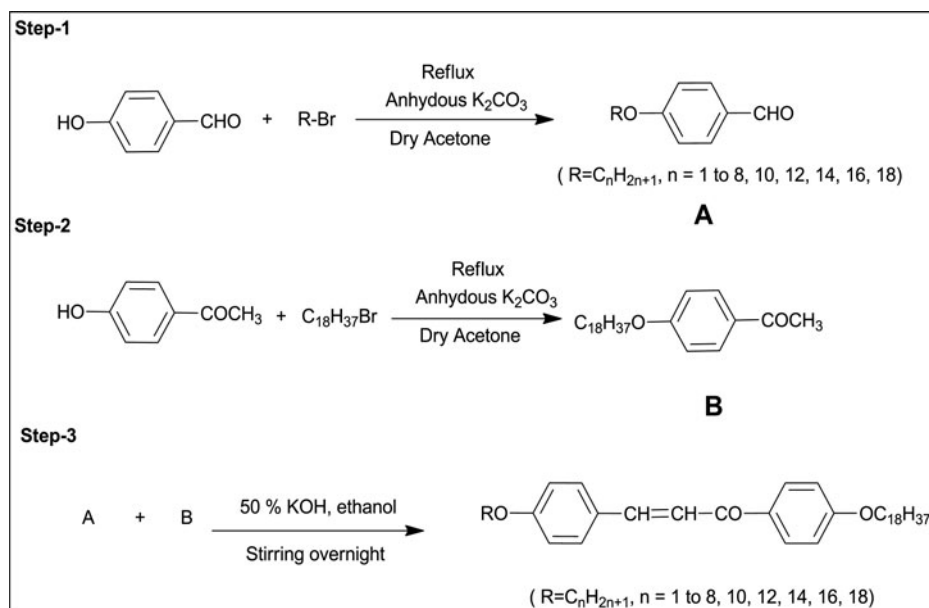
Chalconyl derivatives are well known for their bioactivity as antibacterial, antifungal, anti-malarial, and anticancer compounds [1, 2, 3, 4] but they are relatively less known as liquid crystalline (LC) materials [5] whose potency and utility can be exploited to the benefit of mankind in thermography and LC devices workable at low temperature or room temperature [6, 7, 8]. Thus, the present investigation is planned to understand and establish the effect of molecular structure on LC properties [9, 10, 11, 12] by synthesizing a novel homologous series, which consists of a chalconyl group, which links two phenyl rings, a varying n-alkoxy group $-\text{OR}$ and a fixed $-\text{OC}_{18}\text{H}_{37}(\text{n})$ chain. The study involves synthesis, characterization, transition temperatures, and texture determination by an optical polarizing microscope (POM) equipped with a heating stage. The evaluated thermometric data will be discussed and

interpreted in terms of molecular rigidity and flexibility [13, 14, 15, 16] and will be compared with the structurally similar analogous series to derive the group efficiency order for smectic and nematic, including conclusions. The homologous series with only ester and chalconyl esters have been reported till date [17, 18, 19, 20, 21].

2. Experimental

2.1. Synthesis

4-Hydroxy benzaldehyde was alkylated using suitable alkylating agents (R-X) to give 4-n-alkoxy benzaldehydes (A) by an established method [22]. 4-Octadecyloxy acetophenone (B) is prepared by reported method [23]. Then (A) and (B) were condensed to obtain the final products 4-n alkoxy4'-octadecyloxy phenyl ethylene by an established method [24]. The final products were filtered, washed, dried, and purified until the constant transition temperatures were obtained. The synthetic route to the novel homologous series of ethylene derivatives is shown in Scheme 1.



Scheme 1. Synthetic route to the series.

2.2. Characterization

Representative homologues of the series were characterized by elemental analysis, infrared spectroscopy, and ¹H NMR spectra. IR spectra were recorded on Perkin–Elmer spectrum GX, and ¹H NMR spectra were recorded on a Bruker using CDCl₃ as a solvent. Microanalysis was performed on a Perkin–Elmer PE 2400 CHN analyzer (Table 1). Transition temperature and LC properties (textures) were determined using an optical polarizing microscope equipped with heating stage. Textures of some homologues for the nematic phase were determined by a miscibility method (Table 2).

Table 1. Elemental analysis for butyloxy, heptyloxy, tetradecyloxy, and hexadecyloxy derivatives.

Sr. No.	Molecular formula	Elements found (%)		Elements calculated (%)	
		C	H	C	H
1.	C ₂	80.10	9.50	80.76	10.00
2.	C ₅	80.00	9.80	81.13	10.13
3.	C ₈	80.50	9.45	81.45	10.56
4.	C ₁₀	80.20	9.58	81.64	10.75

3. Analytical data

3.1. IR Spectra (KBr) in cm⁻¹ for pentyloxy, octyloxy derivatives

Pentyloxy: 518, 657, (C-H alkane), 761, 835, polymethylene (-CH₂)_n of -OC₅H₁₁, 835 (-C-H- def. di-substituted-Para), 894 polymethylene (-CH₂-) of -OC₁₈H₃₇, 1074 (-C-H- def. hydrocarbon), 1114 and 1172(-C-O-) Str, 1259 and 1303 and 1321, 1384 (-OCH₂ group in alkyl chain), 1461 (-C-H- Str) 1512, 1581 (-C=C-) Str, 1606,1616 (-C=O in CH=CH- group), 2927 and 3033 (-C-H Str in CH₃).

Octyloxy: 667 (C-H- alkane),725 polymethylene (-CH₂-)n of -OC₈H₁₇, 829 and 894 (-C-H- def. m di-substituted para and ortho aromatic ring), 975 (-C-H- def. hydrocarbon), 1024, 1060, 1116, 1164,1253 (-C-O-) Str of C₁₈H₃₇, 1301 and 1336 (-C-O Str in -(CH₂)_n chain, 1386, 1421 (-C-H- def. in CH₂), (-C=C- aromatic) Str, 1610, 1676 (-C=O in CH=CH- group), 2856 and 2923 (-C-H Str in CH₃).

3.2. ¹HNMR Spectra in CDCl₃ in δ ppm for propyloxy and hexyloxy derivative

Propyloxy: 0.90 (t, -CH₃ of -C₃H₇), 0.88 (t, -CH₃ of -C₁₈H₃₇ chain), 1.29–1.76 (m, n-(CH₂)_n chain of -OC₃H₇), 1.29–1.76 (m, n-polymethylene of -OC₁₈H₃₇ chain), 4.0–4.1 (s, -OCH₂-CH₂- of OC₃H₇ chain), 4.0–4.2 (s, -OCH₂-CH₂- of OC₁₈H₁₇), 6.94–7.5 (s, phenyl ring) and 7.56–7.90 (s, -CO-CH=CH linkage), 7.18–8.11 (s, p-di-substituted phenyl ring).

Hexyloxy: 0.88 (t, -CH₃ of -C₁₈H₃₇), 1.20–1.76 (m, n-(CH₂)_n of -OC₆H₁₃ chain), 1.26–1.76 (m, n-polymethylene groups of -OC₁₈H₃₇), 4.1 (s, -OCH₂-CH₂- of OC₆H₁₃), 4.1–4.4 (s, -OCH₂-CH₂- of OC₁₈H₃₇), 6.94–7.15 (s, substituted benzene), 7.56–7.90 (s, -CO-CH=CH linkage), 7.6–7.8 (s, p-substituted phenyl ring).

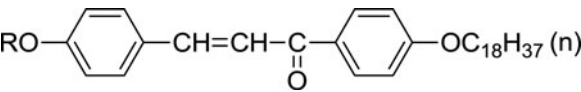
4. Results and discussion

4-n-Alkoxybenzaldehyde and 4-octadecyloxyacetophenon (m.p. 54.0°C, yield 75.69%) are non-mesomorphic components. However, the mesomorphism is induced in the linked-up 11 novel homologues to give thermotropic liquid crystals of low transition temperature. The C₁ and C₂ homologues are non-liquid crystals. The C₃ to C₁₈ homologues are enantiotropic nematogenic, which include C₇ to C₁₈ homologues as anti-tropically smectogenic in addition

Table 2. Textures of nematic phase by miscibility method for C₈, C₁₂, C₁₄, and C₁₈.

Sr. No.	Homologue	Texture
1.	C ₈	Schlieren
2.	C ₁₂	Threaded
3.	C ₁₄	Threaded
4.	C ₁₈	Schlieren

Table 3. Transition temperatures for homologous series



Homologous series: 4-n-alkoxy 4'-octadecyloxyphenyethylenes.

Compound No.	n-alkyl chain C _n H _{2n+1}	Transition temperatures (°C)		
		Smectic	Nematic	Isotropic
1.	C ₁	—	—	95.0
2.	C ₂	—	—	90.0
3.	C ₃	—	72.0	86.0
4.	C ₄	—	63.0	84.0
5.	C ₅	—	49.0	62.0
6.	C ₆	—	41.0	59.0
7.	C ₇	40.0	51.0	64.0
8.	C ₈	45.0	50.0	58.0
9.	C ₁₀	38.0	44.0	54.0
10.	C ₁₂	46.0	52.0	58.0
11.	C ₁₄	55.0	59.0	65.0
12.	C ₁₆	42.0	52.0	70.0
13.	C ₁₈	52.0	61.0	73.0

to nematogenic character. The transition temperatures (Table 3), as determined by POM, were plotted versus the number of carbon atoms present in n-alkyl chain “R” of –OR group and then transition curves Cr-M/I, Sm-N, and N-I are obtained on linking like or related transition points as shown in a phase diagram (Fig. 1), showing their phase behavior of novel series.

Homologous series: 4-n-Alkoxy 4'-octadecyloxyphenyethylenes.

The Cr-M/I transition curve adopts a zigzag path of rising and falling manner with over-all descending manner, and behaved in a normal manner. The Sm-N transition curve rises, passes through maxima at C₁₄ derivative, and descends in a usual established expected manner, but it rises at C₁₈ derivative and shows a very short and sharp odd-even effect. An N-I transition curve descended and then rises abnormally from C₁₂ to C₁₈ derivatives in unexpected manner and exhibited odd-even effect. Thermal stabilities are 52.7°C and 66.6°C for

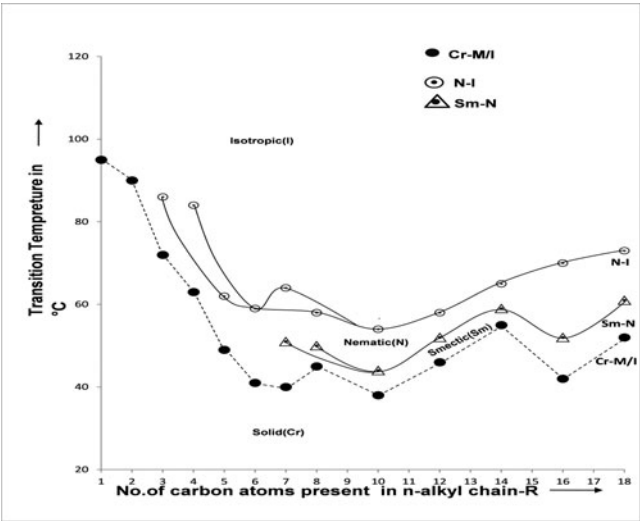


Figure 1. Phase behavior of the series.

smectic and nematic respectively, whose maxima to minimum phase lengths are 05 to 11.0°C and 6 to 21.0°C respectively. Thus, novel homologous series is low melting-type series. Analytical, spectral, and thermal data supported the molecular structures of homologues. Variations in mesogenic properties and behavior from homologue to homologue in the same series are observed with changing number of carbon atoms in n-alkyl chain “R” of –OR group, keeping rest of the molecular part unaltered throughout the series.

The condensation of non-mesomorphs n-alkoxybenzaldehydes with 4-n-octadecyloxy molecule extends molecular lengths, polarity and polarizability, rigidity and flexibility, permanent dipole moment across a long molecular axis, intermolecular end-to-end and lateral attractions, suitable magnitude of dispersion forces and dipole–dipole interaction, etc. These induce resistivity and misalignment of molecules at a 90° or/and less than 90° angle with a plane of floating surface under the influence of exposed thermal vibrations to maintain floating with statistically parallel orientational order and/or with sliding layered molecular arrangement for different range or ranges of temperatures to facilitate only nematic or smectic plus nematic mesophase formation for C₃ to C₁₈ homologues. However, the missing of any sort of mesophase formation in case of C₁ and C₂ homologues is attributed to their high crystallizing tendencies, which arise from low magnitudes of dispersion forces and low magnitudes of dipole–dipole interaction. Thus, abrupt breaking of crystal lattices on heating the sample substance takes place and sharply transform into isotropic liquid without passing through liquid crystalline state. However, on cooling the same, none of the non-mesomorphic homologues C₁ and C₂ exhibited monotropic mesophase in irreversible manner but the homologues from C₃ to C₁₈ on similar cooling from isotropic state exhibit and reappear to nematic and smectic phases. The odd-even effect observed for Sm-N and N-I transition curves is due to the presence of number of carbon atoms as even and odd numbered in n-alkyl chain “R” of –OR group.

The disappearance of odd-even effect for higher homologues of longer n-alkyl chain “R” is attributed to their coiling, bending, flexing, or coupling with principal axes of core structure of respective molecules. Therefore, any unpredictable and unexpected deviations or any minor or major abnormality, which appears in the behavior of transition curve or curves, can be attributed to the unpredictable status of flexible n-alkyl chain “R” and/or –OC₁₈H₃₇ (n) end groups, which may modify the magnitudes of flexibility and magnitudes of intermolecular end-to-end and/or lateral cohesion and/or closeness. Lowering of molecular rigidity by only two phenyl rings bonded through single central bridge lowers the numbers of inter-atomic bonds and bond energy, which reflects the magnitudes of (ΔH) enthalpy change of a molecule, and consequently lowers the molecular thermal resistivity toward exposed thermal vibrations. Therefore, the lowering of transition temperatures, thermal stabilities for smectic and nematic as well as mesophase lengths are observed. The changing trends in mesogenic properties and behavior of present series 1 are compared with structurally similar analogous series X [25] and Y [26] as mentioned in Fig. 2.

Figure 2 represents homologous series 1 of the present investigation as well as structurally analogous X and Y selected for comparative study. Homologous series 1, X, and Y are identical with respect to two phenyl rings and one central bridge –CH=CH–CO– contributing to total molecular rigidity and the left n-alkoxy terminals –OR for the same homologue from series to series, which partly contributes to total molecular flexibility for the same homologue and homologue to homologue in the same series. However, they differ with tailed end group, viz. para –OC₁₈H₃₇ (n), meta –OC₁₆H₃₃ (n), and meta –OC₁₄H₂₉ (n) for the same homologue from series to series and homologue to homologue in the same series, which partly contributes to total molecular flexibility. Thus, variations in mesogenic properties and mesogenic behavior

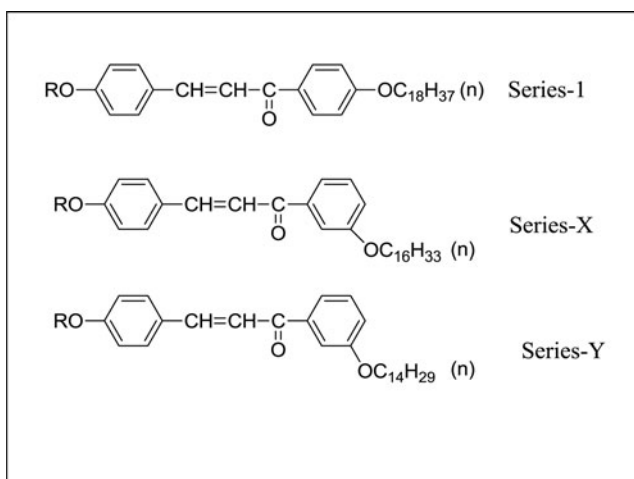


Figure 2. Phase behavior of the series.

can be linked with differing features of their molecular structures, which differ with respect to flexibility of tailed end groups differing by $-\text{CH}_2-\text{CH}_2-$ and their position of substitutions para or meta as shown in Fig. 2. Table 4 represents some evaluated thermometric data indicating mesogenic behavior and the degree of mesomorphism for series 1, X, and Y under comparative study.

Following are clear from Table 3:

- ☐ Homologous series under comparison are predominantly nematogenic and partly smectogenic in enantiotropic and/or monotropic condition.
- ☐ Smectogenic mesomorphism commences from C_6 (series Y) or from C_7 homologue.
- ☐ Nematogenic mesomorphism commences from C_3 homologue in series 1, whereas it commences from C_2 homologue in series X and Y.
- ☐ Thermal stability for smectic is more for the series 1 as compared with series X and Y.
- ☐ Thermal stability for nematic is in increasing order from series 1 to series Y to series X, i.e. series X > series Y > series 1.
- ☐ Total upper mesophase lengths are in decreasing order from series 1 to series X to series Y, i.e. series 1 > series X > series Y.

Homologous series 1 has para substituted $-\text{OC}_{18}\text{H}_{37}(n)$ tailed end and linear geometrical shape, whereas series X and Y have meta-substituted lateral $-\text{OC}_{16}\text{H}_{33}(n)$ and $-\text{OC}_{14}\text{H}_{29}(n)$ tail ended groups. Therefore, length to breadth ratio, intermolecular closeness, molecular and functional group polarities and polarizabilities, permanent dipole moment across the long

Table 4. Relative thermal stability in $^{\circ}\text{C}$.

Series \rightarrow	Para $-\text{OC}_{18}\text{H}_{37}(n)$	Meta $-\text{OC}_{16}\text{H}_{33}(n)$	Meta $-\text{OC}_{14}\text{H}_{29}(n)$
Sm-I or Sm-N	52.7	1.0 to 2.0	1.0 to 2.0
Commencement of smectic phase	(C_7-C_{18})	(Few degrees) (C_7-C_{18})	(Few degrees) (C_6-C_{18})
N-I	66.6	72.6	67.5
Commencement of nematic phase	(C_3-C_{18})	(C_2-C_6)	(C_2-C_5)
	C_3	C_2	C_2
Total mesophase lengths in C^0 minimum to maximum	12.0 to 28.0	5.0 to 21.0	5.0 to 12.0
	$C_{12}-C_{16}$	$C_{18}-C_4$	C_8
			$C_3/C_5/C_{18}$

molecular axis, magnitudes of dipole–dipole interactions, magnitudes of dispersion forces, molecular rigidity and flexibility, and end-to-end and lateral attractions vary more or less in magnitudes for the same homologue from series to series, operating a phenomena of mesomorphism and the degree of mesomorphism. Thus, the two opposing effects of intermolecular attractions due to para- and meta-substituted tail ended n-alkoxy groups play role in facilitating smectic and/or nematic mesophase formation through predominance of either molecular polarity or polarizability factor. Hence, the misalignment of molecules either perpendicular or/and less than 90° on the floating surface causes appearance of smectic or/and nematic-meso phase formation, either in reversible or irreversible manner, to facilitate favorably or unfavorably in enantiotropic or monotropic mode. The early or late commencement of mesophase formation is related with the extent of molecular non-coplanarity with the plane of a floating surface. The para-substituted $-\text{OC}_{18}\text{H}_{37}$ (n), meta-substituted $-\text{OC}_{16}\text{H}_{33}$ (n) as well as $-\text{OC}_{14}\text{H}_{29}$ (n) tail ended n-alkoxy groups are almost equally non-coplanar. Therefore, mesophase smectic and/or nematic commences by the difference of one homologue only. The observed difference can be attributed to the positional difference of tailed n-alkoxy-ended groups, which causes difference in molecular polarizabilities. The observed difference in thermal stabilities for nematic by one or six units is attributed to linear or nonlinear geometrical shape, which is related with the positional status and induced degree of polarizability of n-alkoxy tail-ended group for the same homologue whose magnitudes of energy stored (ΔH) in a molecule vary from series to series. Therefore, the resistivity toward exposed thermal vibrations and their corresponding intensity required different suitable magnitudes of mesophase at different lengths with increasing side chain.

5. Conclusions

- ☐ Homologous series of novel chalconyl derivatives are predominantly nematogenic and partly smectogenic whose total mesophase lengths vary between 12.0 and 28.0°C and low melting type of series.
- ☐ Mesomorphism is very sensitive and susceptible to the molecular structure based on positional substitution of a functional group and its polarizability.
- ☐ Present investigation may be useful for the display device to be operated at room temperatures, and their property as bioactive can be exploited in the interest of mankind.
- ☐ The group efficiency order derived for smectic and nematic on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) total upper mesophase length are as under:

(i) **Smectic**



Nematic



(ii) **Smectic**



Nematic



(iii) Total mesophase length



- ☐ Present investigation has supported and raised the conclusions drawn earlier.

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