



Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Dependence of mesomorphism on molecular rigidity of chalconyl liquid crystals with two phenyl rings

Vinay S. Sharma & R. B. Patel

To cite this article: Vinay S. Sharma & R. B. Patel (2016) Dependence of mesomorphism on molecular rigidity of chalconyl liquid crystals with two phenyl rings, Molecular Crystals and Liquid Crystals, 637:1, 19-27, DOI: 10.1080/15421406.2016.1190502

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1190502



Published online: 10 Nov 2016.



🕼 Submit your article to this journal 🗗



View related articles



View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20



Dependence of mesomorphism on molecular rigidity of chalconyl liquid crystals with two phenyl rings

Vinay S. Sharma and R. B. Patel

Chemistry Department, K. K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India

ABSTRACT

A novel homologues series: $RO-C_6H_4 \cdot CH = CH \cdot CO \cdot C_6H_4 \cdot OC_{16}H_{33}(n)$ (meta) of chalcones with two phenyl rings is synthesized and studied with a view to understanding and establishing the relationship between molecular structure and mesogenic behavior. The series consists of 13 homologues (C1 to C18). Mesomorphism commences from the second member of the series. C2 to C6 homologues are enantiotropicnematic and the rest of the homologues (C7 to C8) are monotropicnematic plus monotropicsmectic. C₁ homologue is nonmesogenic. Transition temperatures were determined by an optical polarizing microscope (POM) equipped with a heating stage. Textures of nematic and smectic phases are threaded, Schlieren or smectic-A, respectively, as judged directly from the heating top of microscopic observations. Thermal, analytical and spectral data confirms the molecular structures. Thermal stabilities for smectic and nematic are few (1 or 2°C) degrees and 72.6°C, respectively. The mesophase lengths are relatively shorter with low mesomorphic transition temperatures (44.0°C to 85.0°C).

KEYWORDS

Chalcones; liquid crystals; monotropy; nematic; smectic

1. Introduction

The combination of potency for thermotropic mesomorphism and biological activity as antibacterial, antifungal, anticancer, antimalarial, etc. is rarely available. Therefore, the present investigation was planned to synthesize chalcone derivatives which act as thermotropic liquid crystals (LC) [1] and biologically active molecules [2]. Which are useful in the benefit of mankind [3–7]. Present work is aimed to understand and establish the relationship between thermotropic mesomorphism and molecular structure [8–12] excluding the study of applications of either thermotropic LC or biological activity. The present study concerns the synthesis of novel LC substances as an homologous series, their characterizations, evaluation of thermometric data and their interpretation in terms of molecular rigidity and flexibility [13–16]; including conclusions in relation with present novel work. Several homologous series have been reported to date [17–23]. The novel compounds are compared with known compounds.

CONTACT R. B. Patel 🐼 roshanpatel770@gmail.com 💼 Chemistry Department, K. K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl. © 2016 Taylor & Francis Group, LLC



Scheme 1. Synthetic route to the series.

2. Experimental

2.1. Synthesis

Alkylation of 4-hydroxy benzaldehyde to give 4-*n*-alkoxy benzaldehyde was carried out by a known method [24] and 3-*n*-alkoxy acetophenone was obtained by alkylation of 3-hydroxy acetophenone by a known method [25].Thus, the chalconyl homologue derivatives (C) were prepared by the usual established method [26] collected and filtered, washed with ethanol solution dried and purified until constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage. Alkyl halides, EtOH, KOH, 3-hydroxy acetophenone, 4-hydroxy benzaldehyde, etc., required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is shown in Scheme-1.

2.2. Characterization

Representative homologues of the series were characterized by elemental analysis, infrared spectroscopy and ¹H NMR spectra. IR spectra were recorded on a Perkin-Elmer spectrum GX, ¹H NMR spectra were recorded on a Bruker using CDCl₃ as solvent. Microanalysis was performed on a Perkin-Elmer PE 2400 CHN analyzer (Table 1). Texture of nematic phase were determined by miscibility method (Table 2). Transition temperatures (Table 3) and LC

Sr. No.	Molecular formula	Elements % found		Elements % Calculated	
		С	Н	С	Н
1	$C_{35}H_{52}O_{3}$	79.72	9.94	80.76	10.00
2	$C_{41}H_{64}O_3$	81.42	10.48	81.45	10.59
3	$C_{43}H_{68}O_3$	81.56	10.62	81.64	10.75
4	$C_{47}H_{76}O_{3}$	81.88	10.94	81.97	11.04

Table 1. Elemental analysis for (1) butoxy (2) decyloxy (3) dodecyloxy and (4) hexadecyloxy derivatives.

Sr. No.	Homologue	Texture
1	C ₇	Threaded
2	C ₁₀	Droplets type
3	C ₁₂	Schlieren
4	C ₁₆	Droplets type

Table 2. Texture of nematic phase of C_7 , C_{10} , C_{12} , C_{16} by miscibility method.

properties (Textures) were observed by using polarizing optical microscope (POM) equipped with heating stage and digital camera.

3. Analytical data

3.1. IR spectra in cm^{-1} for pentoxy&decyloxy derivatives

Pentoxy :2914 (C–H str. of alkane), 2848 (C-H str. of $-(CH_2-)n$ group of $-OC_5H_{11}$ alkyl chain, 1600–1660 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene), 1510, 1560 (C=C str. of aromatic ring), 999 (C–H bending of alkene), 1178 (C–O str. of ether linkage), 1288, 1246 (C–O str. of carbonyl group), 776Polymethylene (-CH₂-) of $-OC_{16}H_{33}$, 678 Polymethylene (-CH₂-)*n* of $-OC_5H_{11}$, 824(–C-H- def. m di-substituted-Para), IR data confirms the molecular structure.

Decyloxy :2916 (C–H str. of alkane), 2850 (C–H str. of $-(CH_2-)n$ group of $-OC_{10}H_{21}$ group, 1600–1660 (C=O str. of carbonyl group of chalconyl group), 1604(C=C str. of alkene), 1579 (C=C str. of aromatic ring), 1004, (C-H bending of alkene), 1190 (C-O str. of ether linkage), 1240, 1256 (C–O str. of carbonyl group), 776 Polymethylene (-CH₂-) of $-OC_{16}H_{33}$, 823 (–C-H- def. m di-substituted-Para), IR data confirms the molecular structure.

3.2. ¹HNMR spectra in CDCl₃ in δ ppm for hexyloxy&octadecyloxy derivative

 $\begin{array}{l} \textbf{Hexyloxy: } 0.88 \ (t, 6H, -CH_3 \ of \ polymethylene \ -C_6H_{13} \ and \ -C_{16}H_{33}), \ 1.79 \ (p, 10H, CH_3-CH_2-CH_2-CH_2-CH_2-of \ -OC_6H_{13} \ and \ -OC_{16}H_{33}), \ 1.28 \ (m, 14H \ -CH_2-CH_2-CH_2-of \ -OC_6H_{13} \ and \ -OC_{16}H_{33}), \ 1.31 \ (q, 8H, \ -CH_2-CH_3), \ 4.06 \ (t, 4H, \ -OCH_2-CH_2-), \ 7.59 \ (d, 2H, \ -CH=CH-), \ 7.43, \ (d, 2H, \ -CH=CH-), \ 7.44, \$

		Transition temperatures in °C		
Sr. no	R = n-alkyl group	Smectic	Nematic	lsotropic
1	C ₁	_	_	86.0
2	C2	_	69.0	82.0
3	C ₃	—	62.0	76.0
4	C_{4}^{2}	—	50.0	71.0
5	C_5	—	48.0	68.0
6	C_6	—	50.0	66.0
7	C ₇	(42.0)	(48.0)	58.0
8	C ₈	(47.0)	(54.0)	59.0
9	C ₁₀	(44.0)	(56.0)	62.0
10	C ₁₂	(42.0)	(53.0)	60.0
11	C ₁₄	(47.0)	(55.0)	64.0
12	C ₁₆	(49.0)	(56.0)	65.0
13	C ₁₈	(54.0)	(59.0)	72.0

Table 3. Transition temperature in °C.

() indicates monotropy.



Figure 1. Phase behaviors of series.

7.28 & 7.83 (4H, meta substituted phenyl ring), 7.56 & 7.97 (4H, phenyl ring with alkoxy chain). NMR data confirms the molecular structure.

Octadecyloxy: 0.88 (t, 6H, -CH₃ of -C₁₈H₃₇ and -C₁₆H₃₃), 1.80(p, 10H, CH₃-CH₂-CH₂-CH₂-CH₂-CH₂ of -OC₁₈H₃₇ and -OC₁₆H₃₃), 1.28 (m, polymethylene 18H -CH₂-CH of -OC18H37 and -OC16H33), 1.34 (q, 8H, -CH2-CH3), 4.05(t, 4H, -OCH2-CH2-), 7.59 (d, 2H, -CH=CH-),7.43, 7.28 &7.83 (4H, meta substituted phenyl ring), 7.56 & 7.97 (4H, phenyl ring), 6.95 & 7.62 (4H, phenyl ring with alkoxy chain). NMR data confirms the molecular structure.

4. Results and discussion

4-*n*-alkoxy benzaldehydes are nonmesomorphic but linking with metan-hexadecyloxyace tophenone generates mesomorphic properties from the C_2 to C_{18} homologues. The novel homologues consist of two phenyl rings bonded through one central bridge -CH=CH-COand exhibit mesomorphism. The C₂ to C₆ homologues are enantiotropicnematic whereas, and the C₇ to C₁₈ homologues are monotropically nematogenic and also monotropically smectogenic. A phase diagram showing phase behaviors (Fig. 1) is obtained by plotting transition temperatures against the number of carbon atoms present in n-alkyl chain "R" of left –OR group and then on linking like or related points, transition curves Cr-N/I, N-I or I-N and N-Sm are obtained. Cr-N/I transition curve adopted zigzag path of rising and falling with overall descending tendency as series is ascended and behaved in normal manner. N-I or I-N transition curve descended upto C₇ homologue and then rises by about ten to twelve degree and behaved in normal manner. Monotropic N-Sm transition curve rises, then falls at C12 homologues and then again ascended upto C_{18} member of a series, under discussion, Thus N-Sm transition curve also behaved in normal manner. N-I/I-N and N-Sm transition curves adopted very short and narrow odd-even effects for one or two homologues. Odd-even effects for N-I and N-Sm transition curves are observed upto C_4 and C_9 homologues, respectively, and then a single transition curves are followed for higher homologues of longer n-alkyl chain



Figure 2. POM image of (a) Sm C phase of C_{10} homologue monotropically at 44°C, (b) Nematic phase of C_{16} homologue at 56°C during cooled condition.

"R" of –OR group. Thermal stability for smectic is few degree (1 or 2°C) but thermal stability fornematic is 72.6°C. Mesophase length ranges between 5.0 and 21.0°C. Normally the sequence of appearing mesophase in ester or azoester series is first monotropy and then enantiotropy, but; in case of presently invested chalconyl (-CH=CH–CO-) central group containing two phenyl ring consisted homologous series is appeared as first enantiotropy and then monotropy which is reversal to normal behavior; due to presence of only chalconyl central group. The variations in thermotropic mesomorphic properties from homologue to homologue in the same series appeared, with changing value of "R" of –OR group.

The molecular length of 4-*n*-alkoxy benzaldehyde increases by linking 3-*n*-hexadecyloxy acetophenone, which upgrades the molecular rigidity and flexibility to suitable and favorable magnitudes of intermolecular cohesion and closeness to induce nematic and smectic phase in enantiotropic or monotropic manner. The exhibition of smectogenic and nematogenic characters are attributed to the corresponding molecular arrangements as sliding layered organization due to lamellar packing of molecules in preoccupied lattices of rigid crystals to induce smectogenic property and the stastically parallel orientational order of molecules due to end to end favorable intermolecular attractions and closeness as well as suitable magnitudes of polar and polarizable nature of flexible end groups of laterally substituted group. Fig. 2 shows the POM image of C10 homologue at its transition temperature during cooled condition at 44°C, while comp. C16 shows nematic mesophase at 56°C monotropically, respectively.

The presence of laterally substituted flexible longer *n*-alkoxy group $(-OC_{16}H_{33})$ (n) widens the molecular width which causes reduction in the magnitudes of attractions but suitable to induce enantiotropic/monotropic mesophase or inducing mesophases reversibly or irreversibly. Meta substituted $-OC_{16}H_{33}(n)$ group helps in building sliding layered molecular arrangement on cooling the isotropic mass of a sample substance commencing from C_7 to C_{18} homologues in irreversible manner or in monotropic condition, and lowers the transition temperatures upto 44.0°C. The exhibition of minor or shorter odd–even effects in mesogenic transition curves of a phase diagram is due to the addition of methylene unit in *n*-alkyl chain "R" of –OR end group. The disappearance of odd–even effect from and beyond a homologue to which curves for odd and even members are merging into each other for higher homologues of longer *n*-alkyl chains "R" of –OR and–OC₁₆H₃₃(*n*) flexible groups which is attributed to the coiling or bending or flexing or coupling of *n*-alkyl chain with the major axis of core structure of a molecule which causes resultant suitable magnitudes of intermolecular cohesion to



Figure 3. Structurally similar series.

induce mesophase or mesophases. The absence of mesogenic character in C_1 homologue is due to the low magnitudes of dispersion forces and low magnitudes of dipole-dipole interactions. The changing trend in mesogenic properties from homologue to homologue in the same series is attributed to the changing number of carbon atoms present in n-alkyl chain "R" of -OR group and unexpected status of *n*-alkyl chain or end groups of a molecule. The reverse deviating effect from normal sequence of appearing monotropy and then enantiotropy is attributed to the unexpected status of n-alkyl chains which affected molecular lengths from homologue to homologue in the same series which alters molecular polarity and polarizability. Some thermometric properties and degree of mesomorphism of presently investigated homologous series-1 and a structurally similar homologous series-X [27] as shown in Fig. 3 are compared.

Figure 4 shows the space-filling model of energy minimized for series1 and series X respectively. Homologous series-1 and X are identical with respect to two phenyl rings bonded through -CH=CH-CO- which contributes the total rigidity of series-1 and the part of rigidity of series-X to its total rigidity. However, they differ with respect to absence and presence of $-C_6H_4$ -COO- unit of molecules of series-1 and X contributing to molecular rigidity as well as tail ends $-OC_{16}H_{33}(n)$ and $-NO_2$ contributing to molecular flexibilities due to the differing



Figure 4. Space filling diagram of series 1 and X.

Series→	Series-1 (-OC ₁₆ H ₃₃) Absent of -C ₆ H ₄ .COO-	Series-X (-NO ₂) Presence ofCOO-
Sm-N or N-Sm or Sm-I	1–2°C	125.0
Commencement of smectic phase	$(C_7 - C_{18})$	$(C_6 - C_{12})$
N-I or I-N	72.6	167.4
Commencement of nematic phase	$(C_2 - C_6)$	$(C_3 - C_{16})$
Mesophaselength (Sm $+$ N) in $^{\circ}$ C	05.0°C to 21.0°C C ₁₈ C ₄	09.0 to 65.0 C ₄ C ₆

Table 4. Thermal stability in°C

molecular polarity and polarizability. Thus, variations in mesogenic properties and the degree of mesomorphism will depend upon the magnitudes of differing features between series-1 and X. i.e. rigidity played by $-C_6H_4$ -COO- and the flexibility varied due to $-OC_{16}H_{33}(n)$ and $-NO_2$ lateral group of series-1 and X, together which operates the differing behaviours between series-1 and X for the same homologue and homologue to homologue in the same series.

Following Table 4 represents some thermometric properties in comparative manner as under.

Above Table 3 shows the following.

- Homologous series of present investigation -1 and X under comparative study are smectogenic plus nematogenic.
- Sequential order of mesophase is as enantiotropy first (C_2 to C_6) and then monotropy from C_7 to C_{18} homologue in case of series-1, whereas monotropic transitions are absent for analogous series-X. Its smectogenic and nematogenic transitions are enantiotropic.
- Smectogenicmesophase commences from C₇ and C₆homologue respectively for series-1 and X.
- Nematogenicmesophase commences from C₂ and C₃ homologue respectively for series-1 and X.
- Thermal stabilities and mesophaselengths of series 1 are relatively much lower than corresponding analogous series-X chosen for comparison.

The exhibition of smectogenic and nematogenic characters by the chalconyl series-1 and a chalconyl ester series-X is attributed to the optimum magnitudes of dispersion forces and optimum magnitudes of dipole-dipole interactions controlling suitable magnitudes of anisotropic forces of intermolecular cohesion and closeness to induce smectic plus nematic phase in either reversible or irreversible manner. The early or late commencement of smectic and nematic phase are depended upon the extent of noncoplanarity of a molecule. Homologous series 1 and X under comparison are equally noncoplanar due to meta substituted tail end groups whose group polarity and polarizability differed and therefore the smectic and nematicmesophases commences by the difference of one homologue, i.e., C_7 or C_6 and C_2 or C_3 . The lower values of thermal stabilities and mesophaselengths of series-1 as compared to series-X are attributed to the weakening of the suitable magnitudes of inter molecular cohesion by reducing molecular rigidity by $-C_6H_4$.COO- unit which is related with energy stored (ΔH) by a molecules of homologous series at the time of formation. Thus, it is obvious that a molecule of same homologue from series to series having lower rigidity will resist, exposed thermal vibrations at lower transition temperatures and will facilitate low degree of mesophaselengths of and low thermal stabilities. Thus, lowering of molecular rigidity results in lowering of thermal stabilities and simultaneously the degree of mesomorphism. The variations in mesogenic properties for the same homologue from series to series are due to the changing tail end or lateral group; its polarity and polarizability and overall molecular rigidity / flexibility keeping rest of the molecular part unaltered, whereas, variations in mesogenic properties from homologue to homologue in the same series is due the sequentially changing numbers of methylene unit or units at n-alkyl chain 'R' of –OR keeping tail or lateral group unaltered throughout a series.

5. Conclusions

- Novel homologous series of only chalconyl (-CH=CH-CO-) central bridge as linking group with side chain based two phenyl rings and two end or lateral groups are predominantly nematogenic and partly smectogenic whose thermal stabilities and the mesophaselengths are low and it is as low ordered melting type.Chalconyl group is generally nematogenic and bioactive which is useful for devices to be operated at low temperature or room temperature, as well as its bioactivity is very useful in agriculture products of good quality by its antibacterial and antifungal activity. Here, in present article, we successfully synthesized the homologous series which shows LC properties as lower temperature as present demand.
- The group efficiency order derived on the basis of (i) thermal stabilities (ii) commencement of mesophase and (iii) upper and lower mesophaselengths for smectic and nematic are as under.
- (i) **Smectic**:

 $-NO_2 > -OC_{16}H_{33}$ (n) Nematic: $-NO_2 > -OC_{16}H_{33}$ (n)

- (ii) Smectic: $-NO_2 > -OC_{16}H_{33}$ (n) Nematic: $-OC_{16}H_{33}$ (n) $> -NO_2$
- (iii) Smectic / Nematic - $NO_2 > -OC_{16}H_{33}(n)$

Acknowledgments

Authors acknowledge thanks to Dr. R. R. Shah, principal and management of K. K. Shah Jarodwala Maninagar Science College, Ahmedabad. Authors are also thankful to Dr. A.V. Doshi, Ex-principal of M.V.M. Science and Home Sci. College, Rajkot for his constant support, inspirations, valuable suggestions and comments, as and when needed during the course of present investigation. Authors thank to NFDD Centre for the analytical and spectral services.

References

- [1] Reintitzer, F. (1988). Monatshefte, 9, 421.
- [2] Griffin, R. J., Srinivasan, S., Bowman, K., Calvert, A. H., Curtin, N. J., Newell, D. R., Pemberton, L. C., & Golding, B. T. (1988). J. Med. Chem., 41, 5256.
- [3] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). Displays, 29, 458-463.
- [4] Naruma, S. (2001). Display, 22, 1.
- [5] Calliste, C. A., Bail le, J.C., Trouilas, P., Poug, C., Chulia, A.J., & Duroux, L. J. (2001). Anticancer Res., 21, 3949–3956.
- [6] Gaikwad, P., & Desai, T. (2013). IJPRR, 2(12), 40-52.

- [7] Fischer, P., & Finkelman, H. (1988). Prog. Colloid. Polym. Sci., 111, 127.
- [8] Henderson, P. A., Niemeyer, O., & Imrie, C. T. (2001). Liq. Cryst., 28, 463-472.
- [9] Imrie, C. T. (1999). Struct. Bond, 95, 149–192.
- [10] Brehmer, M., & Zentel, R. (1994). Mol. Cryst. Liq. Cryst., 243, 353.
- [11] Gray, G.W. (1962). Molecular Structures and Properties of Liquid Crystals, Academic Press: London.
- [12] Imrie, C. T., & Luckhrust, G. R. (1988). In: Liquid Dimers and Oligomers in Handbook of Liquid Crystal, Low Molecular Liquid Crystals, Vol. 2B, Demus, D., Goodby, J. W., Gray, G. W., Spiess, H., & Vill, V. (Eds.), pp. 801–833. Wiley-VCH: Weinheim.
- [13] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & McDonell, D. G. (1993). Liq. Cryst., 15, 123.
- [14] Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, A. (1992). Adv. Matter, 4, 285.
- [15] Hird, M., Toyne, K. J., Gray, G. W., & Day, S. E. (1993). Liq. Cryst., 14, 741.
- [16] Collings, P. J., & Hird, M. (1998). Introduction of Liquid Crystals Chemistry and Physics, Taylor and Francis Ltd.: U.K.
- [17] Demus, D. (1988). Mol. Cryst. Liq. Cryst., 165, 45-84.
- [18] Demus, D. (1988). Liq. Cryst., 5, 75-110.
- [19] (i) Suthar, D. M., & Doshi, A. V. (2013). Mol. Cryst. Liq. Cryst., 575, 76–83. (iv)Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). Mol, Cryst. Liq. Cryst., 552, 104–110.
- [20] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). Mol. Cryst. Liq. Cryst., 527, 51-58.
- [21] (a) Sharma, V. S., & Patel, R. B. (2015). *ILCPA, Scipress Ltd.*, 60, 182–191. (b) Sharma, V. S., & Patel, R. B. (2015). *ILCPA, Scipress Ltd.*, 59, 115–123. (c) Sharma, V. S., Solanki, R. B., Patel, P. K., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 625(1), 137–145.
- [22] Sharma, V. S., & Patel, R. B. (2015). ILCPA, Scipress Ltd., 58, 144-153.
- [23] Patel, B. H., & Doshi, A. V. (2015). Mol. Cryst. Liq. Cryst., 605, 61-69.
- [24] Hasan, A., Abbas, A., & Akhtar, M. N. (2011). Molecule, 16, 7789-7802.
- [25] Nikitin, K. V., & Andryukhova, N. P. (2004). Can. J. Chem., 82, 571-578.
- [26] Furniss, B. S., Hannford, A. J., Smith, P. W.G., & Tatchell, A. R. (Revisors). (1989). Vogel's Textbook of Practical Organic Chemistry (4thEdn.), Longmann Singapore Publishers Pvt. Ltd.: Singapore, 563–649.
- [27] Chaudhari, R. P., & Doshi, A. V. (2013). Mol. Cryst. Liq. Cryst., 570, 109-116.