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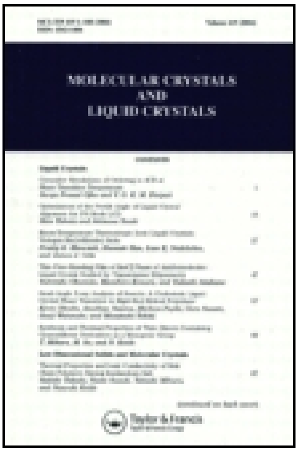

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 22 Apr 2013.

To cite this article: Himanshu S. Bhatt , Purvang D. Patel & Jayrang S. Dave (2013) Synthesis of Liquid Crystals with Lateral Substituents in Central and Terminal Benzene Cores and Their Mesomorphic Characterization, Molecular Crystals and Liquid Crystals, 575:1, 104-111, DOI: 10.1080/15421406.2013.768497

To link to this article: http://dx.doi.org/10.1080/15421406.2013.768497

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Mol. Cryst. Liq. Cryst., Vol. 575: pp. 104–111, 2013
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.768497

Synthesis of Liquid Crystals with Lateral Substituents in Central and Terminal Benzene Cores and Their Mesomorphic Characterization

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A new homologous series consisting of 12 homologues central azo, and ester linkage with chloro lateral group at central and methyl group at the terminal benzene ring is synthesized and their mesomorphic properties are studied. All the homologues are mesogenic in nature. All the compounds are exhibiting enantiotropic nematic phase; no homologues shows smectic phase even in monotropic form. To evaluate the effect of lateral chloro group at central benzene ring and methyl group at terminal benzene ring, the present series is compared with structurally related homologous series. The structure of the synthesized compounds is characterized by standard spectroscopic method, viz., IR, UV, NMR, and MASS.

Keywords Azo-ester mesogen; lateral chloro group; lateral methyl group; mesomorphism; nematic

Introduction

Lateral substituents play an effective role in mesogenic properties of a mesogenic compound as it makes molecules broad. Studies on the effect of lateral substitution have been carried out by several researchers. A literature survey indicates that generally the mesophase range of mesogens with lateral substituent is less than that for laterally unsubstituted mesogens [1–11]. Mesomorphic behaviors of mesogens depends on the molecular structures of molecules and molecular forces arising; therefore, a slight change in the molecular geometry brings about considerable change in its mesomorphic properties [1–9,12–17]. Literature survey indicates that the study of lateral substitution at central and terminal benzene ring is rare, however [6–8,14,17]. Our group has reported the effect of lateral substitution on mesomorphic properties of fluoro aniline derivatives [7] and also lateral methyl substitution on azo-ester mesogens [18]. Keeping this in view, we have synthesized a new homologous series consisting of azo and ester central linkages and lateral chloro group at central and methyl group at terminal benzene core in order to study the effect of lateral substitution on mesomorphism at different lateral position on different benzene cores.

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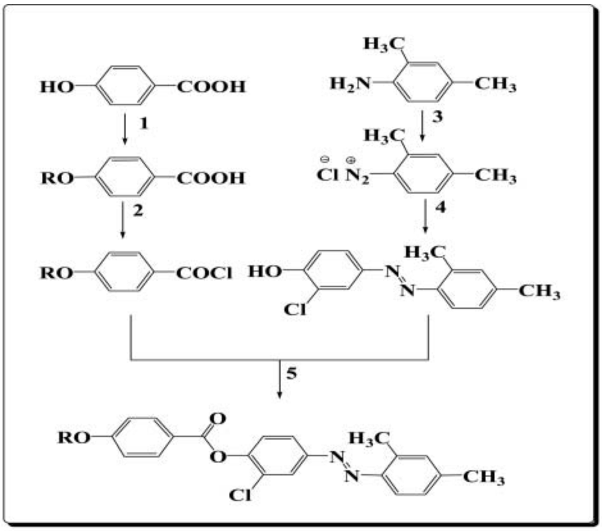
Experimental

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, 2, 4-dimethylaniline, 2-Chloro phenol were of Loba grade, used as received. Solvents were dried and distilled prior to use. Structure of the synthesized compounds were confirmed by the spectroscopic techniques, viz., mass spectra were recorded on Applied biosystems API 2000 mass spectrometer; infrared (IR) spectra were recorded on a Shimadzu IR-408, and nuclear magnetic resonance (NMR) spectra were measured on a Varian mercury-300 spectrometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL optical polarizing microscope provided with a Kofler heating stage.

1. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the reported method [9].
2. 4-Hydroxyphenylazo-2′, 4′-dimethylbenzene, and 3-methyl-4-hydroxyphenylazo-2′, 4′-dimethylbenzene were prepared by a known method [10].
3. The Series I, namely 4-(4′-n-alkoxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethylbenzenes were synthesized by adding drop wise a cold solution of 3-chloro-4 hydroxyphenylazo-2″, 4″-dimethylbenzene, in dry pyridine to a cold solution of 4-n-alkoxybenzoyl chlorides. The mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 cold HCl and the separated solid was filtered and column chromatographed on silica gel (60–120 mesh) with 2% ethyl acetate - petroleum ether (60°C–80°C) (2:98) mixture as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallized repeatedly from methanol until constant transition temperatures were obtained. These are recorded in Table 2. The mass analyses of C7 member (Series I) were found to be satisfactory. The synthetic route of the series is shown in Scheme 1.



$R = C_nH_{2n+1}$ n = 1 to 8, 10,12,14,16

(1) Alcohol, KOH, n-RBr, (2) $SOCl_2$, (3) HCl, $NaNO_2$, H_2O/0-5 °C, (4) 2-Chloro phenol, aq.NaOH, at 0--10° C, pH 8--12, (5) Dry Pyridine, 1:1 cold HCl

Scheme 1. Synthetic route.

IR Data

FTIR (Nujol, KBr pellets, cm^{-1}) were recorded on a Shimadzu IR-408.

Compounds 7: -4-(4′-n-heptyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethyl benzene

2952–2858 (C—H St, Alkyl CH_3, SP^3 hybridization), 1730 (—C=O— St. of ester), 1602 (—N=N— St.), 1570–1500 (—C=C— St. of Aromatic ring), 1477(—C—H bending of $—CH_2—$), 1250(Aromatic ether St.), 1061(—C—O— St. of ester), 893(strong —C—H— bending for 1:2:4 tri substituted benzene ring), 725 (weak —C—H— bending for $—(CH_2)_6—$) cm^{-1}.

Compounds 8: -4-(4′-n-octyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethyl benzene

2954–2857 (C—H St, Alkyl CH_3, SP^3 hybridization), 1735 (—C=O— St. of ester), 1604 (—N=N— St.), 1573–1502 (—C=C— St. of Aromatic ring), 1478(—C—H bending of $—CH_2—$), 1256(Aromatic ether St.), 1065(—C—O— St. of ester), 890(strong —C—H— bending for 1:2:4 tri substituted benzene ring), 728 (weak —C—H- bending for $—(CH_2)_7—$) cm^{-1}.

Compounds 10: -4-(4′-n-decyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethyl benzene

2952–2856 (C—H St, Alkyl CH_3, SP^3 hybridization), 1733 (—C=O— St. of ester), 1602 (—N=N— St.), 1577–1500 (—C=C— St. of Aromatic ring), 1477(—C—H bending of $—CH_2—$), 1253(Aromatic ether St.), 1063(—C—O— St. of ester), 899(strong —C—H— bending for 1:2:4 tri substituted benzene ring), 722 (weak —C—H— bending for $—(CH_2)_9—$) cm^{-1}.

Compounds 12: -4-(4′-n-dodecyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethyl benzene

2954–2858 (C—H St, Alkyl CH_3, SP^3 hybridization), 1733 (—C=O— St. of ester), 1604 (—N=N— St.), 1574–1505 (—C=C— St. of Aromatic ring), 1482(—C—H bending of $—CH_2—$), 1248(Aromatic ether St.), 1067(—C—O— St. of ester), 895(strong —C—H— bending for 1:2:4 tri substituted benzene ring), 725 (weak —C—H— bending for $—(CH_2)_{11}—$) cm^{-1}.

UV Data

The UV absorption data for the solution of Series I compounds (7, 8, 10, 12) in ethyl acetate at 25°C are recorded in Table 1. For compounds (7, 8, 10, 12) of Series I, Wavelength ranging from 450 and 341 corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively.

Table 1. UV data of compounds (7, 8, 10, 12)

	(UV) Wavelength	
N	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
7	444.50	341.00
8	445.50	341.50
10	450.50	341.50
12	442.00	341.50

Table 2. Transition temperature °C of Series I. Series I: -4-(4′-n-alkyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethylbenzenes

	Transition temperature °C	
R = n-Alkyl group	Nematic	Isotropic
Methyl	121	163
Ethyl	118	160
Propyl	109	153
Butyl	98	141
Pentyl	92	139
Hexyl	80	133
Heptyl	79	126
Octyl	84	129
Decyl	72	124
Dodecyl	75	102
Tetradecyl	72	93
Hexadecyl	63	85

NMR Data

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm, standard TMS) were recorded on Varian mercury 300 ($CDCl_3$, 300 MHz, δ, ppm, standard TMS)

Compound 10: -4-(4′-n-decyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethyl benzene.

$\delta = 0.88$ (t, 3H, aliphatic $-CH_3$), 1.25-1.83 (m, 18H, 9($-CH_2$-)), 1.85 (Qunt, 2H, $-COCH_2$), 2.39 (s, 3H, Ar-CH_3) 2.70 (s, 3H, Ar-CH_3), 4.04 (t, 3H, $-OCH_2$), 6.98–8.21 (m, 11H, Ar-H)

Mass Analysis

MS (FAB+): m/z for $C_{28}H_{31}ClN_2O_3$: calculated (M+1), 278.2; found (M+1), 279.0

Results and Discussion

In the present investigation, a new homologous series of 12 compounds, viz., 4-(4′-n-alkyloxybenzoyloxy) 3-chlorolphenyl azo-2″, 4″-dimethylbenzenes (Series I), was synthesized and their mesomorphic properties were studied.

All the 12 homologs of the series are mesogens; the nematic phase commences from the very first derivative and remains up to the last hexadecyl derivative synthesized. Figure 1 shows the plot of transition temperatures against number of carbon atoms in the n-alkoxy chain; it indicates that Cr-M transitions show overall falling tendency with a jump at the C8 derivative; the N-I curve shows overall falling tendency with a clear rising tendency at C8 and C10 homologs as the series is ascended. The nematic phase of the series shows marble texture.

The present series is compared with structurally related homologous series and Figure 3 shows 3D molecular structure of those series in comparison from ChemDraw Ultra 8.0

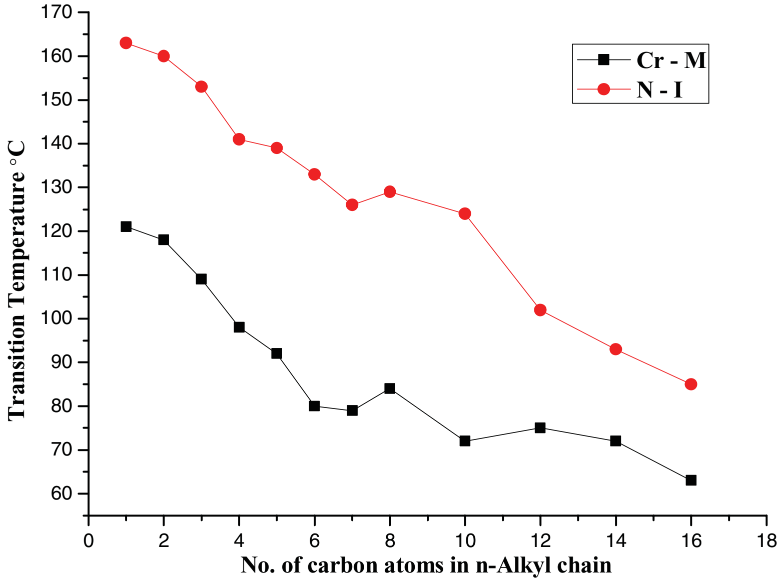


Figure 1. Series I: 4-(4′-n-alkyloxybenzoyloxy)-3-chlorophenylazo-2″, 4″-dimethylbenzenes.

Software; table 3 indicates thermal stabilities of that series in comparison. Figure 4 shows optical polarising microscopic images of C7 and C10 homolog of the series.

Series I is purely nematogenic in nature as it does not exhibit smectic mesophase till C16 derivative studied, whereas Series A [2] and B [18] exhibit smectogenic behavior at C16 and C10 derivative respectively. Series C [19] is again purely nematogenic in behavior. The purely nematogenic behavior of the entire Series I can be due to the presence of two lateral substituents namely —Cl in central benzene ring and —CH_3 in terminal benzene ring

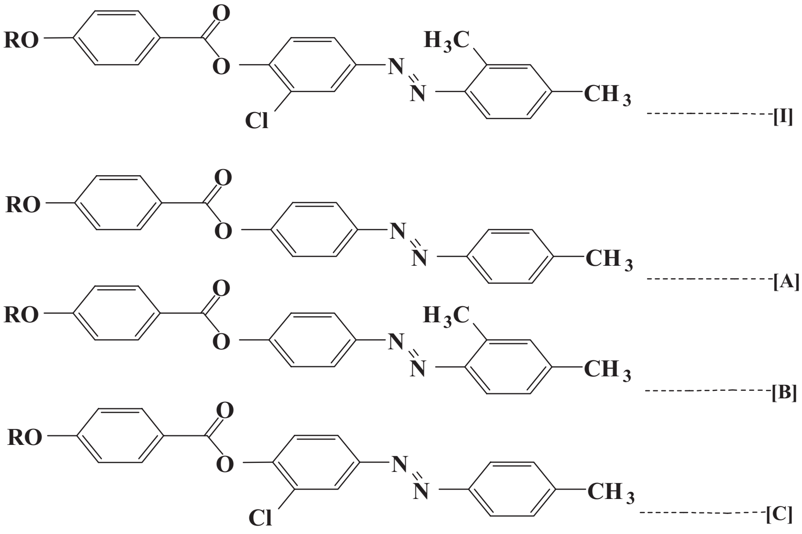


Figure 2. Show molecular structure of the series in comparison.

Table 3. Average thermal stabilities °C

Series	Smectic-isotropic °C or smectic-nematic °C	Nematic-isotropic °C	Commencement of smectic mesophase
1	—	129 (C_1-C_{16})	—
A	106.5 (C_{10}-C_{16})	242 (C_1-C_8)	C_{10}
B	62 (C_{16})	155.6 (C_1-C_{16})	C_{16}
C	—	164.2 (C_3-C_{16})	—

which broadens the molecules and makes molecule not to remain along major molecular axis. Series A has higher N-I thermal stability as compared with other structurally related homologous Series I, B, C; this can be due to no lateral substituent in Series A; similarly Series A has higher S-I thermal stabilities than Series B due to the same reason.

The introduction of the lateral chloro and methyl groups in Series I change the molecular conformation and broaden the molecules, which decreases the transition temperatures and thermal stabilities of smectic and nematic mesophase [13,8,9]. This factor is a direct result of an increase in the thickness of the molecule [11]. The increased dissymmetry resulting from the lateral chloro and methyl group leads to less effective molecular packing in the crystal lattice and, therefore, lowers the crystal to mesophase transition temperature as shown in Table 2[9]. Thus, the effect of substitution, which leads to an increase in molecular breadth, is that the long narrow molecules will be forced further apart so reducing the strength

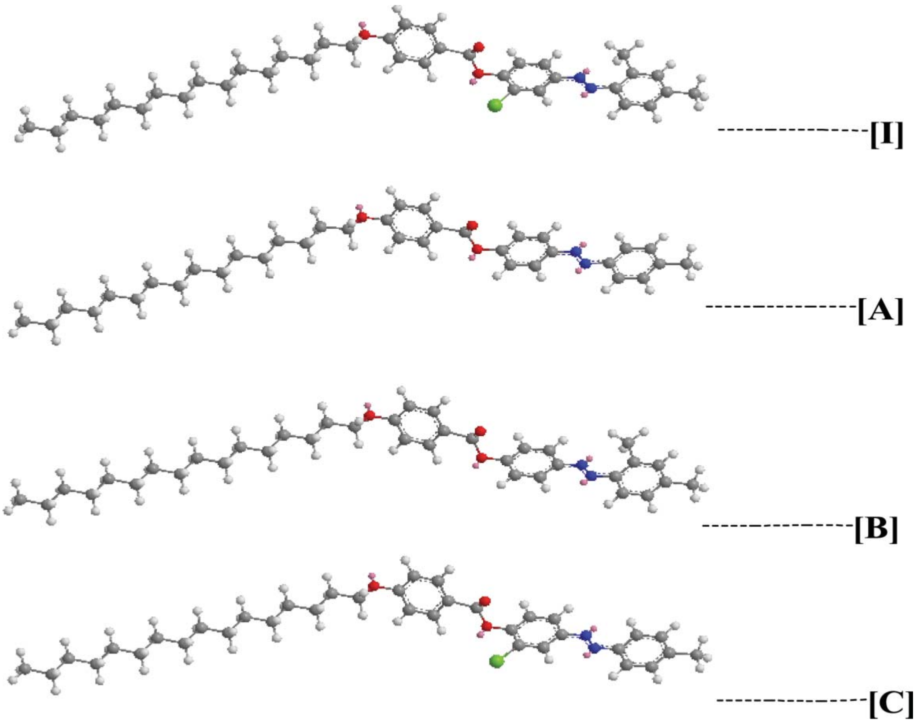


Figure 3. 3D molecular structure of the series in comparison from ChemDraw Ultra 8.0 Software.

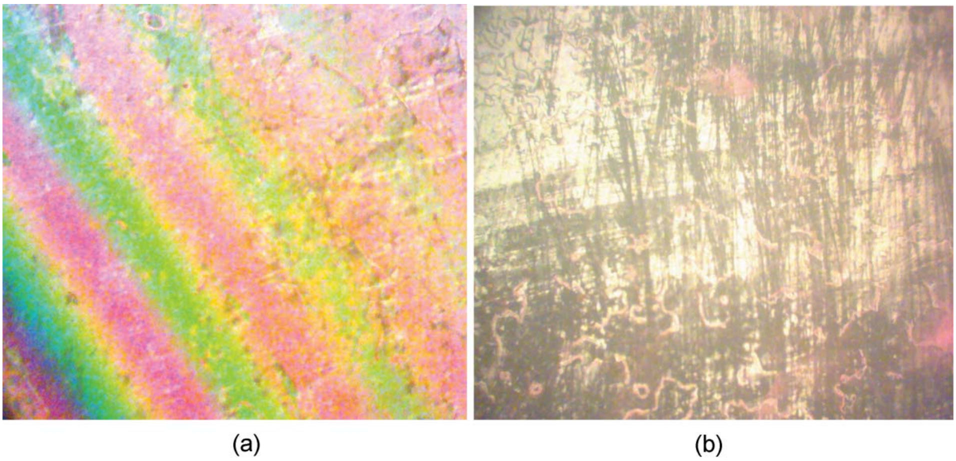


Figure 4. (a) Marble texture of nematic phase of compound C7 Series I at 92°C on cooling. (b) Marble texture of the nematic phase of Compound C10 Series I at 98°C on cooling.

of the intermolecular lateral attractions. Both smectic and nematic mesophases depend to a greater or lesser extent on these cohesive forces to maintain the parallel orientation of the molecules. Therefore, substitution leading to an increase in molecular breadth will decrease the smectic and nematic thermal stabilities, which is actually found in the present Series I (2).

Conclusion

A new homologous series consisting of 12 homologs with central azo and ester linkage and with chloro and methyl lateral groups at central and terminal benzene rings, respectively, is synthesized and their mesomorphic properties are studied. All the compounds exhibit only enantiotropic nematic phase with marble texture; the present series does not exhibit smectic mesophase which may be due to the presence of two lateral substitutions, namely $-Cl$ and $-CH_3$ in central and terminal benzene rings, respectively. Present homologous series is compared with other structurally related homologous series to evaluate the effect of lateral substitutions on mesomorphism.

Acknowledgment

The authors are thankful to the Head of the Applied Chemistry Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara, for providing the laboratory facilities as well as analytical instruments facilities.

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