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

Synthesis and Characterization of bis[n-(4-benzoyloxy) Benzylidene{n(n-di-/tri-alkoxy)benzoyl}-hydrazinato]nickel(II) Complexes Displaying Liquid Crystalline Columnar Phases

M. Nurul Abser [a], M. Manzurul Karim [a], Abu Kauser [a], Rabeya Parvin [a], M. Elias Molla [a], Zenifer Yeasmin [a], Wajdi Michel Zoghaib [b], Zainab Al-Rawahi [b], Carlo Carboni [c] & Ghalib Al-Saidi [d]

[a] Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

[b] Department of Chemistry, Sultan Qaboos University, Al-Khod, Sultanate of Oman

[c] Department of Physics, Sultan Qaboos University, Al-Khod, Sultanate of Oman

[d] Department of Food Science & Nutrition, Sultan Qaboos University, Al-Khod, Sultanate of Oman

Version of record first published: 18 Jan 2013.

To cite this article: M. Nurul Abser , M. Manzurul Karim , Abu Kauser , Rabeya Parvin , M. Elias Molla , Zenifer Yeasmin , Wajdi Michel Zoghaib , Zainab Al-Rawahi , Carlo Carboni & Ghalib Al-Saidi (2013): Synthesis and Characterization of bis[n-(4-benzoyloxy) Benzylidene{n(n-di-/tri-alkoxy)benzoyl}-hydrazinato]nickel(II) Complexes Displaying Liquid Crystalline Columnar Phases, Molecular Crystals and Liquid Crystals, 571:1, 9-18

To link to this article: http://dx.doi.org/10.1080/15421406.2012.726008

Mol. Cryst. Liq. Cryst., Vol. 571: pp. 9–18, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.726008

Synthesis and Characterization of *bis*[*n*-(4-benzoyloxy) Benzylidene{*n*(*n*-di-/tri-alkoxy)benzoyl}-hydrazinato]nickel(II) Complexes Displaying Liquid Crystalline Columnar Phases

M. NURUL ABSER,[1] M. MANZURUL KARIM,[1] ABU KAUSER,[1] RABEYA PARVIN,[1] M. ELIAS MOLLA,[1] ZENIFER YEASMIN,[1] WAJDI MICHEL ZOGHAIB,[2,*] ZAINAB AL-RAWAHI,[2] CARLO CARBONI,[3] AND GHALIB AL-SAIDI[4]

[1]Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh
[2]Department of Chemistry, Sultan Qaboos University, Al-Khod, Sultanate of Oman
[3]Department of Physics, Sultan Qaboos University, Al-Khod, Sultanate of Oman
[4]Department of Food Science & Nutrition, Sultan Qaboos University, Al-Khod, Sultanate of Oman

A series of materials based on the aroylhydrazinatonickel (II) complex is synthesized and characterized. The molecule in the materials consist of two 4-benzoyloxy-benzene groups and two benzene rings having two or three alkoxy chains containing 6, 8, 10, and 12 carbon atoms attached at the azomethine moiety. The synthesis, characterization by NMR and the phase sequence observed by DSC and polarized light microscopy are presented. Most of the compounds in the series display columnar phases in the temperature range between 100°C and 200°C. The phases observed and their temperature ranges are discussed in terms of the number and position of attached alkoxy chains.

Keywords Columnar; dendritic growth; discotic; metallomesogen

1. Introduction

The incorporation of heterocyclic rings as core centers in the generation of mesogenic materials has been widely investigated during the more than 30 years of discotic liquid crystal research [1,2]. Five- or six-membered heterocyclic rings have been studied extensively due to their structural variety and known chemistry. Good mesomorphic behavior often resulted from such structures which can be attributed to their electronic properties and polarizability [3].

In parallel to the use of heterocyclic rings, metal-containing liquid crystals (metallomesogens) have received considerable attention for more than a decade now [4,5]. Numerous

*Address correspondence to Wajdi Michel Zoghaib, Department of Chemistry, Sultan Qaboos University, P.O. Box 36, Al-Khod 123, Sultanate of Oman. Tel.: +968-24142472; Fax.: +968-24141469. E-mail: zoghaibw@squ.edu.om

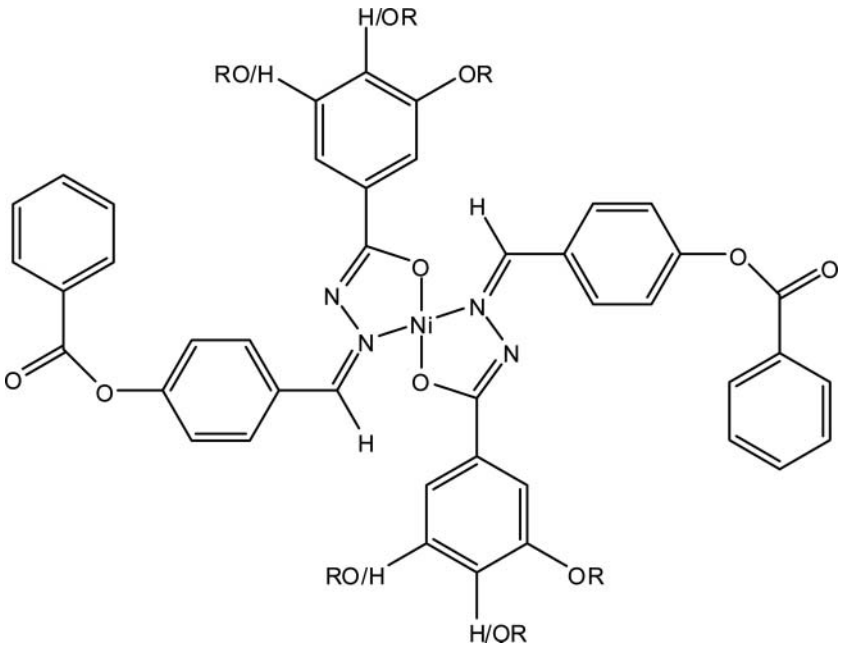


Figure 1. The general schematic diagram of the molecules in the series of materials synthesized.

transition metal-containing liquid crystalline materials with varying molecular structures were synthesized and their mesomorphic properties investigated.

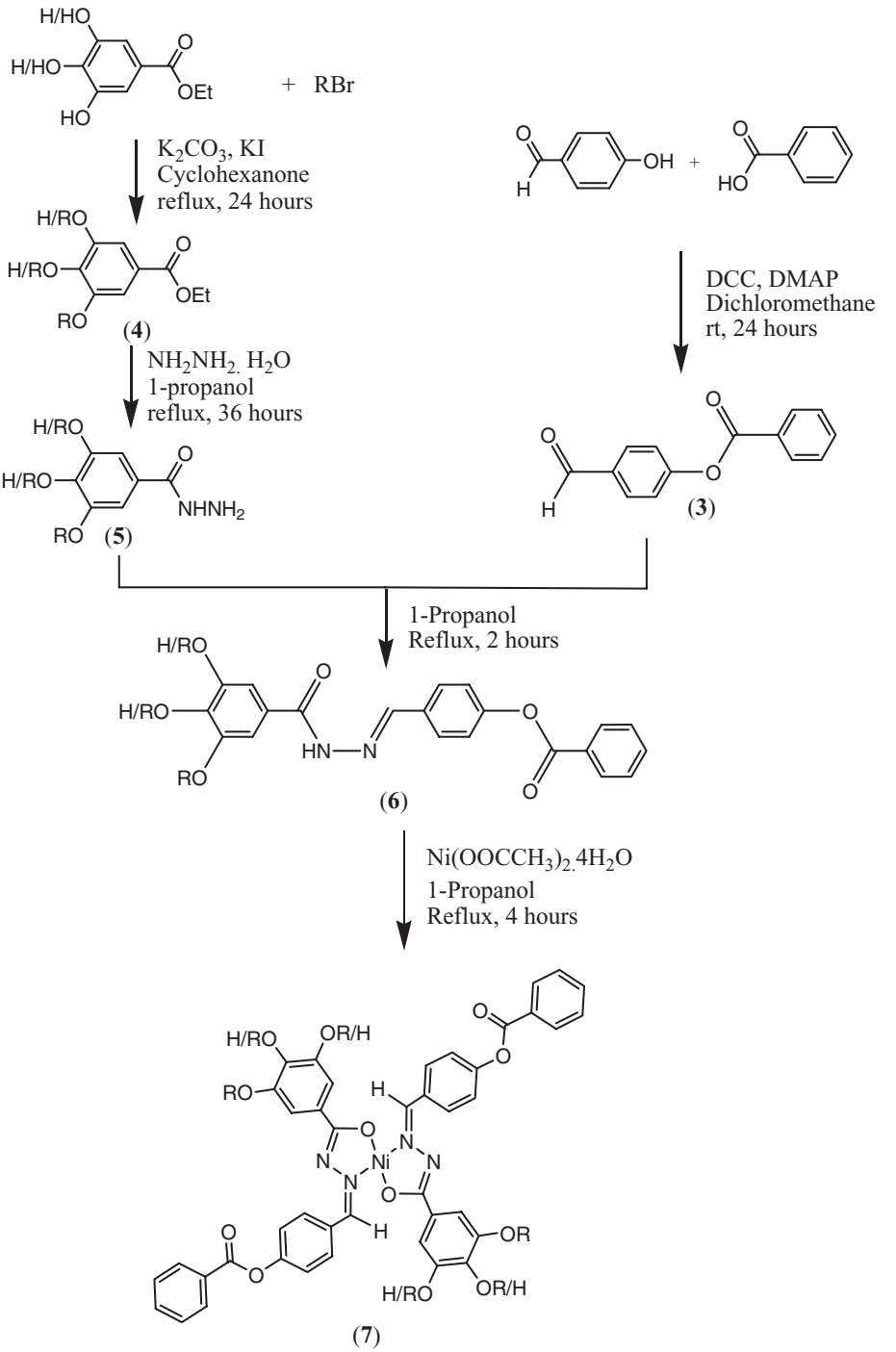
Numerous metallomesomorphic materials with varying length branched chains (ethers or esters) attached to the rigid core were prepared and investigated [6]. In the case of rod-like liquid crystals, an increase in the chain length leads to more organized mesophase structures [7,8]. Thus nematic phases are more stable with short chains, while smectic phases are thermodynamically favored when longer chains are present; compounds with intermediate chain length sometimes show polymorphism.

The present paper is an investigation of the formation of discotic liquid–crystal phases with molecules based on the aroylhydrazinatonickel (II). The general schematic diagram of molecules in the series presented here is given in Fig. 1. The molecule consists of the aroylhydrazinatonickel (II) complex with two 4-benzoyloxy-benzene groups; benzene rings attached at the azomethine moiety have either two alkoxy chains at either positions 3 and 4 or 3 and 5 or three alkoxy chains at positions 3, 4, and 5. Individual alkoxy chains are composed of 6, 8, 10, or 12 carbon atoms.

The position and length (6, 8, 10, and 12 carbon atoms) of the alkoxy chains are the parameters varied in the present study. Throughout this study, materials in the series will be labeled by the number and position of the alkoxy chain and the number of carbon atoms in the chain.

2. Synthesis

The complexes have been synthesized following the method summarized in Scheme 1 and details provided in references [9–13]. The reaction of benzoic acid with



Scheme 1. Generalized synthesis of title compounds.

Table 1. Calculated and experimental C, H, and N elemental analysis

Structure	Calculated C, H, and N	Experimental C, H, and N
3,4-C_6	$C_{66}H_{78}N_4NiO_{10}$ C: 69.17; H: 6.86; N: 4.89	$C_{66}H_{78}N_4NiO_{10}$ C: 69.12; H: 6.83; N: 4.85
3,5-C_6	$C_{66}H_{78}N_4NiO_{10}$ C: 69.17; H: 6.86; N: 4.89	$C_{66}H_{78}N_4NiO_{10}$ C: 69.10; H: 6.82; N: 4.86
3,4,5-C_6	$C_{78}H_{102}N_4NiO_{12}$ C: 69.58; H: 7.64; N: 4.16	$C_{78}H_{102}N_4NiO_{12}$ C: 69.51; H: 7.58; N: 4.13
3,4-C_8	$C_{74}H_{94}N_4NiO_{10}$ C: 70.64; H: 7.53; N: 4.45	$C_{74}H_{94}N_4NiO_{10}$ C: 70.45; H: 7.45; N: 4.38
3,5-C_8	$C_{74}H_{94}N_4NiO_{10}$ C: 70.64; H: 7.53; N: 4.45	$C_{74}H_{94}N_4NiO_{10}$ C: 70.41; H: 7.44; N: 4.36
3,4,5-C_8	$C_{90}H_{126}N_4NiO_{12}$ C: 71.37; H: 8.38; N: 3.70	$C_{90}H_{126}N_4NiO_{12}$ C: 71.14; H: 8.31; N: 3.59
3,4-C_{10}	$C_{82}H_{110}N_4NiO_{10}$ C: 71.86; H: 8.09; N: 4.09	$C_{82}H_{110}N_4NiO_{10}$ C: 71.75; H: 8.07; N: 4.05
3,5-C_{10}	$C_{82}H_{110}N_4NiO_{10}$ C: 71.86; H: 8.09; N: 4.09	$C_{82}H_{110}N_4NiO_{10}$ C: 71.75; H: 8.07; N: 4.05
3,4,5-C_{10}	$C_{102}H_{150}N_4NiO_{12}$ C: 72.79; H: 8.98; N: 3.33	$C_{102}H_{150}N_4NiO_{12}$ C: 72.59; H: 8.90; N: 3.30
3,4-C_{12}	$C_{90}H_{126}N_4NiO_{10}$ C: 72.91; H: 8.57; N: 3.78	$C_{90}H_{126}N_4NiO_{10}$ C: 72.55; H: 8.51; N: 3.75
3,5-C_{12}	$C_{90}H_{126}N_4NiO_{10}$ C: 72.91; H: 8.57; N: 3.78	$C_{90}H_{126}N_4NiO_{10}$ C: 72.61; H: 8.50; N: 3.81
3,4,5-C_{12}	$C_{114}H_{174}N_4NiO_{12}$ C: 73.96; H: 9.47; N: 3.03	$C_{114}H_{174}N_4NiO_{12}$ C: 73.66; H: 9.42; N: 3.01

4-hydroxybenzaldehyde in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) in dichloromethane at room temperature for 24 hours gave 4-benzoyloxybenzaldehyde **3** as a white solid. Alkylation (using 1-bromo alkanes) of di-/tri-hydroxybenzoates was performed in refluxing cyclohexanone by using anhydrous K_2CO_3 as the base and KI as a catalyst. The di-/tri-alkoxybenzoates **4** were converted to the corresponding hydrazines **5** by reacting with excess hydrazine hydrate in refluxing 1-propanol. The Schiff bases **6** of the hydrazines were generated by condensation of **5** with **3** in refluxing 1-propanol and were used in situ for complexation with nickel (II) acetate. The nickel (II) complexes **7** were isolated in good yield as orange–red solid by recrystallization from dichloromethane/acetone mixture and their purity was confirmed by the 1H NMR and C, H, and N elemental analysis (Table 1). All the isolated nickel complexes have good solubility in common organic solvents.

The 1-bromoalkanes, ethyl 3,4-di-hydroxybenzoate, methyl 3,5-di-hydroxybenzoate, ethyl 3,4,5-tri-hydroxybenzoate, benzoic acid, 4-hydroxybenzaldehyde DCC, and DMAP were obtained from ACROS Organics chemicals (Geel, Belgium) and were used as purchased so were the other conventional reagents. 1-Propanol was distilled over calcium oxide. A precoated silica gel aluminum plate (Silica gel 60, F-254, 0.25 mm) from E-Merck was used for analytical TLC, while flash column chromatography was done over silica gel Merck 60 (230–400 mesh) for purification.

2.1. 4-Benzoyloxybenzaldehyde (3)

Equimolar quantities of benzoic acid and 4-hydroxybenzaldehyde in the presence of DCC and a catalytic amount of DMAP (0.1 gm) in dichloromethane (25 mL) were stirred for 24 hours at room temperature. After filtration and evaporation a white solid was obtained, which was recrystallized from methanol.

IR (KBr); ν, cm^{-1}: 2847, 2811 (aliphatic, C–H), 1736 (C=O, ester), 1697 (C=O, aldehyde), 1595, 1502, 1450 (aromatic, C=C), 1207, 1157, 1058 (C–O), 878, 816, 708, 677, 517.

^{1}H-NMR ($CDCl_3$); δ, ppm: 10.01 (1H, s, CHO), 8.19 (2H, dd, 7.2 Hz, 1.2 Hz, C_6H_5), 7.96 (2H, d, C_6H_4, 8.4 Hz, C_6H_4), 7.66 (1H, dd, J = 7.2, 1.2 Hz, C_6H_5), 7.53 (2H, dd, J = 7.2, 7.2 Hz, C_6H_5), and 7.38 (2H, d, 8.4 Hz, C_6H_4).

2.2. Alkylation of Di-/tri-hydroxybenzoates: Synthesis of Compounds (4)

Alkylation of di-/tri-hydroxybenzoates was achieved by following a general procedure. Details of methyl 3,5-di-decyloxybenzoate are given here. While for 3,5-dialkoxy derivatives the methyl ester (methyl 3,5-di-hydroxybenzoate) was used, for 3,4-dialkoxy and 3,4,5-trialkoxy derivatives, ethyl 3,4-di-hydroxybenzoate and ethyl 3,4,5-tri-hydroxybenzoate were used, respectively.

A mixture of methyl 3,5-di-hydroxybenzoate (9.2 g, 55 mmol), 1-bromodecane (24.8 g, 112 mmol), anhydrous potassium carbonate (23 g, 165 mmol), and catalytic amount of KI (ca. 1 g) in cyclohexanone (100 mL) was refluxed for 24 hours. Solvent was removed under reduced pressure and the residual mass was treated with water (75 mL), extracted with dichloromethane (4 × 30 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo. Crystallization of the crude product from hexane/dichloromethane (2:1) gave the pure methyl 3,5-di-decyloxybenzoate as white solid. Yield: 90%.

IR (KBr); ν, cm^{-1}: 2923(s), 2851(m) (saturated, C–H), 1723(s) (C=O), 1601(m), (aromatic, C=C), 1472(w), 1443(m), 1393(w), 1325(m), 1240(m), 1165(s), 1129(w), 1055(m), 1007(w), 860(w), and 762(w).

^{1}H-NMR ($CDCl_3$); δ, ppm: 7.16 (2H, d, J = 2.2 Hz, C_6H_3), 6.63 (1H, dd, J = 2.2 Hz, C_6H_3), 3.96 (4H, t, J = 6.5 Hz, –OC$\underline{H}_2$CH$_2$–), 3.9 (3H, s, OC$\underline{H}_3$), 1.77 (4H, m, –OCH$_2$C$\underline{H}_2$CH$_2$), 1.44–1.26 (36H, m, –O(CH$_2$)$_2$(C$\underline{H}_2$)$_7$CH$_3$), and 0.88 (6H, t, J = 6.5 Hz, –O(CH$_2$)$_9$C$\underline{H}_3$).

2.3. Synthesis of Acid Hydrazides (5)

The acid hydrazides were synthesized by following a general procedure; representative details for 3,5-di-decyloxybenzoylhydrazine are given here.A mixture of methyl 3,5-di-decyloxybenzoate (10 g, 22.3 mmol) and hydrazine hydrate (10 g, 200 mmol) was refluxed in 1-propanol (50 mL) for 36 hours. The reaction mixture was cooled to room temperature and treated with water (100 mL). The white solid thus formed was filtered and dried under suction. It was then recrystallized from ethanol to give the title compound as a white solid. Yield: 75%.

IR, (KBr); υ, cm^{-1}: 3370(w), 3312(w) (N–H), 2920(s), 2851(s) (saturated, C–H), 1642(s) (C=O), 1595(s), 1518(s) (aromatic, C=C), 1470(w), 1390(w), 1358(m), 1304(w), 1179(s), 1055(w), 874(w), 837(w), 766(w), 685(w), 517(w).

^{1}H-NMR ($CDCl_3$); δ, ppm: 7.41 (1H, bs, –CON$\underline{H}$N$\underline{H}_2$), 6.83 (2H, d, J = 2 Hz, C_6H_3), 6.57 (1H, dd, J = 2 Hz, C_6H_3), 4.1 (2H, bs, –CONHN$\underline{H}_2$), 3.95 (4H, t, J = 6.5 Hz, –OCH$_2$C$\underline{H}_2$–), 1.76 (4H, m, –OCH$_2$C$\underline{H}_2$CH$_2$–), 1.20–1.40 (28H, m, –OCH$_2$CH$_2$(C$\underline{H}_2$)$_7$CH$_3$), and 0.88 (6H, t, J = 6.5 Hz, –O(CH$_2$)$_9$CH$_3$).

2.4. Synthesis of the Complex (7)

A mixture of 4-benzoyloxybenzaldehyde (**3**) and appropriate alkyloxybenzoylhydrazine (**5**) in 1:1 molar ratio was refluxed in 1-propanol (20 mL) for 2 hours, after which nickel (II) acetate (0.5 mol equivalent) was added to the reaction mixture, and refluxing was continued for another 4 hours. The reaction mixture was cooled to room temperature and the resulting yellow solid was collected by filtration; washed thoroughly with water and ethanol. The crude product was dissolved in dichloromethane and passed through a short column of silica eluting with hexane/dichloromethane (2:1, v/v), and subsequently re-crystallized from dichloromethane/acetone to afford the complexes **7** as orange–red solids.

Complex **3,4-C_{10}**:

Yield: 59%.

^{1}H-NMR ($CDCl_3$); δ, ppm: 8.43 (2H, d, 8.8 Hz, C_6H_4), 8.22 (2H, d, J = 7.6 Hz, 1 Hz, C_6H_5) 7.67 (1H, dd, J = 7.6 Hz, 1 Hz, C_6H_5), 7.59–7.47 (4H, overlap peaks), 7.37 (2H, d, J = 8.8 Hz, C_6H_4), 7.26 (1H, s, N=C<u>H</u>) 6.88 (2H, d, J = 8.8 Hz, C_6H_3), 4.0 (4H), 1.84 (4H), 1.48 (4H), 1.25 (24H), and 0.87 (6H).

Complex **3,5-C_{10}**:

Yield: 56%.

^{1}H-NMR ($CDCl_3$); δ, ppm: 8.43 (2H, d, 8.8 Hz, C_6H_4), 8.22 (4H, dd, 8.5 Hz, 1.3 Hz, C_6H_5), 7.65 (1H, d, J = 7.4 Hz, 2 Hz, C_6H_5), 7.54 (2H, dd, J = 7.6 Hz, J = 7.0, C_6H_5), 7.36 (2H, d, 8.8 Hz, C_6H_4), 7.27 (1H, s, N=CH), 7.11 (2H, d, 2 Hz, C_6H_3), 6.56 (1H, dd, 2 Hz, 2 Hz, C_6H_3), 3.99 (4H), 1.79 (4H), 1.46 (4H), 1.37 (24H), and 0.92 (6H).

Complex **3,4,5-C_{10}**:

Yield: 47%.

^{1}H-NMR ($CDCl_3$); δ, ppm: 8.40 (2H, d, 8.8 Hz, C_6H_4), 8.23 (4H, dd, 8.0 Hz, 1.0 Hz, C_6H_5), 7.6 (1H, dd, J = 7.4 Hz, 2 Hz, C_6H_5), 7.50 (2H, dd, J = 7.4 Hz, J = 1.2 Hz, C_6H_5), 7.36 (2H, d, 8.8 Hz, C_6H_4), 7.25 (1H, s, N=CH), 7.21 (2H, s, C_6H_2), 4.0 (6H), 1.88–1.72 (6H), 1.54–1.47 (6H), 1.34–1.31 (36H), and 0.93–0.88 (9H).

3. Structural Characterization of the Complexes by ^{1}H-NMR

The H^1 NMR spectra were obtained on a *Bruker Avance* 400 MHz spectrometer (Bruker Biospin, Switzerland). For the ^{1}H-NMR measurements, residual $CHCl_3$ in $CDCl_3$ was employed as the internal standard and assigned as 7.26 ppm downfield from TMS. Assignments were made on the basis of chemical shift, multiplicity, and ortho, meta, and para substitution patterns.

All the complexes displayed sharp peaks in their ^{1}H-NMR spectra and are consistent with their structure.

Complexes **3,4,5-C_n**: The protons of the C_6H_2 ring give a singlet at around δ 7.21 for proton **a;** the protons of the C_6H_4 ring give two separate doublets of equal intensity and coupling constant 8.8 Hz at around δ 8.40 and δ 7.36; the protons of the C_6H_5 ring give three separate signals, two double doublets at δ 8.23 for proton **b** and δ 7.50 for proton **b**, while the proton **d** resonates at δ 7.60.

Complexes **3,5-C_n**: The protons of the C_6H_3 ring give a double doublet at δ 6.56 for proton **a**, while proton **b** resonates as a doublet at δ 7.11; the protons of the C_6H_4 ring give two separate doublets of equal intensity and coupling constant 8.8 Hz at δ 8.43 and δ 7.36; the protons of the C_6H_5 ring give three separate signals, two double doublets at δ 8.22 for proton **c** and δ 7.55 for proton **d**, while the proton **e** resonates at δ 7.36.

Complexes **3,4-C*n***: The proton **c** of the ring C_6H_3 gives a doublet at around δ 6.88, the other two protons **a** and **b** of this ring give overlapped peak with that of proton **e** of the ring C_6H_5; the protons of the C_6H_4 ring give two separate doublets of equal intensity and coupling constant 8.8 Hz at δ 8.43 and δ 7.36; the protons **d** of the C_6H_5 ring give a doublet at δ 8.22; proton **f** resonates at δ 7.55, while the signal from proton **e** overlaps that of protons **a** and **b** at δ 7.59–7.47.

Table 1 displays the calculated versus experimental C, H, and N elemental analysis for all 12 compounds in thestudy.

4. Phase Sequences

The transition temperatures on heating were observed by Differential Scanning Calorimetry (DSC); phase identification was done on cooling by using a polarized light microscope. The phase changes were observed by varying the temperature at a rate of 0.5°C per minute. For the polarized light microscopy observations, the specimen was placed between a clean microscope slide and a cover slip; no alignment treatment was applied to the glass. The specimen was seared by applying a force parallel to the plane of the cell on the cover slip. A summary of the observed phase sequences is given in Table 2, while Table 3 specifically shows the transition to isotropic for each of the materials. In Table 2, the symbol *Cr* is loosely used to refer to the solid phase observed at room temperature, it was not always possible to ascertain from the optical observations if the phase is crystalline or glass. The label X is used for a mesophase that can be easily sheared but could not be unequivocally identified from the observed texture between crossed polarizers. We have labeled $Col_?$ as a columnar phase where there is no well-defined symmetry in the observed dendritic growth on cooling from the isotropic phase.

Table 2. Phase sequences of the compounds in the series. The uncertainty on transition temperatures is of the order of 2°C

Label	R	Phase sequence on heating
3,4-C_6	$C_6H_{13}O$	$Cr \xrightarrow{196} Col_h \xleftrightarrow{250} I$
3,4-C_8	$C_8H_{17}O$	$Cr \xrightarrow{76} X \xrightarrow{98} Col_h \xleftrightarrow{208} I$
3,4-C_{10}	$C_{10}H_{21}O$	$Cr \xrightarrow{104} X \xleftrightarrow{198} I$
3,4-C_{12}	$C_{12}H_{25}O$	$Cr \xrightarrow{124} X \xleftrightarrow{184} I$
3,5-C_6	$C_6H_{13}O$	$Cr_1 \xrightarrow{187} Cr_1 \xrightarrow{190} Col_h \xleftrightarrow{282} I$
3,5-C_8	$C_8H_{17}O$	$Cr \xrightarrow{159} Col_h \xleftrightarrow{260} I$
3,5-C_{10}	$C_{10}H_{21}O$	$Cr \xrightarrow{122} Cr_1 \xrightarrow{182} Col_h \xleftrightarrow{242} I$
3,5-C_{12}	$C_{12}H_{25}O$	$Cr \xrightarrow{118} Cr_1 \xrightarrow{137} Col_h \xleftrightarrow{224} I$
3,4,5-C_6	$C_6H_{13}O$	$Cr \xrightarrow{257} Col_? \xleftrightarrow{259} I$
3,4,5-C_8	$C_8H_{17}O$	$Cr \xrightarrow{152} Col_? \xleftrightarrow{233} I$
3,4,5-C_{10}	$C_{10}H_{21}O$	$Cr \xrightarrow{106} Col_? \xleftrightarrow{222} I$
3,4,5-C_{12}	$C_{12}H_{25}O$	$Cr \xrightarrow{50} Col_? \xleftrightarrow{207} I$

Table 3. Transition temperatures to isotropic phase

Label	Transition to isotropic (°C)	Label	Transition to isotropic (°C)	Label	Transition to isotropic (°C)
3,4-C_6	250	3,5-C_6	282	3,4,5-C_6	259
3,4-C_8	208	3,5-C_8	260	3,4,5-C_8	233
3,4-C_{10}	198	3,5-C_{10}	242	3,4,5-C_{10}	222
3,4-C_{12}	184	3,5-C_{12}	224	3,4,5-C_{12}	207

As for most discotic materials, the spontaneous alignment of the columnar phase on slow cooling from the isotropic phase between glass plates is homeotropic with the axis of the columns perpendicular to the cover slip. Plate 1 shows some of the textures observed. The typical dendritic growth of the columnar phase was better observed with slightly uncrossed polarizers.

The **3,4-C_n** materials with $n = 6$ and $n = 8$ display a Col_h phase on cooling from the isotropic phase. Dendritic growth with the well-defined hexagonal symmetry characteristic of the Col_h phase [14,15] is observed (insert in photo A, plate 1). The Col_h phase grows with

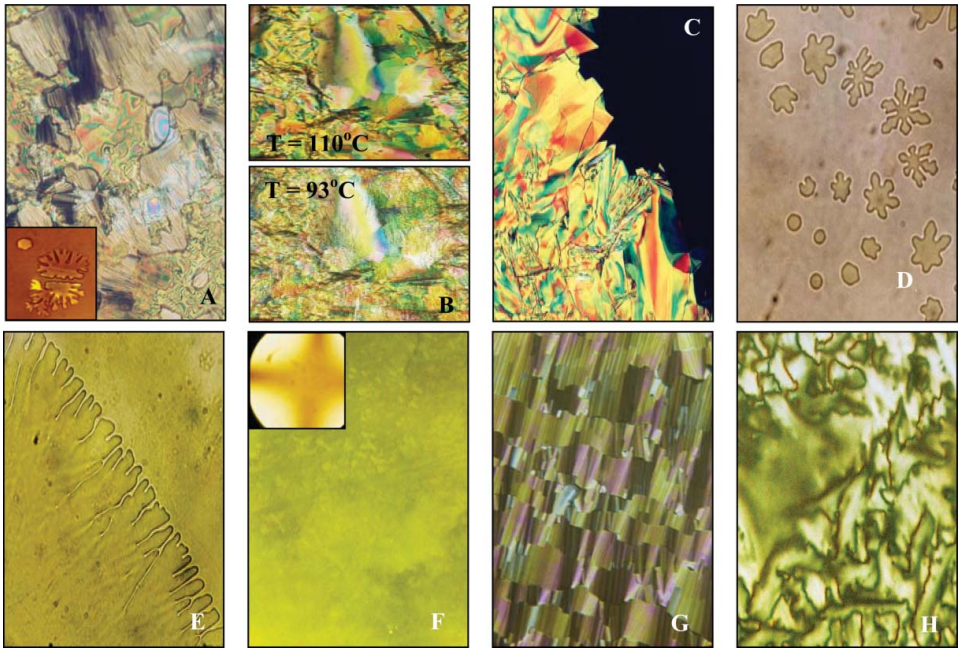


Plate 1. Some of the textures observed in the series of materials. *A*: **3,4-C_6** at 248°C after shearing. The insert shows the dendritic growth at 258°C; *B*: the crystal transition in **3,4-C_{10}**, above the transition at 110°C and below the transition at 93°C; *C*: **3,4-C_{12}** growing in the isotropic liquid at 184°C, *D*: Hexagonal dendritic growth of **3,5-C_{10}** at 244°C. *E*: **3,4,5-C_{10}** growth from isotropic phase 222°C. *F*: **3,4,5-C_{10}** homeotropic alignment at $T = 177$°C; the insert shows the conoscopic figure obtained from the texture by using a Bertrand lens. *G*: **3,4,5-C_{10}** texture obtained after shearing at 177°C. *H*: **3,4,5-C_{10}** at 100°C, the texture cannot be sheared.

the axis of the column normal to the glass plates giving a dark orange uniform color to the sample. However, if a gentle shear is applied to the sample, the orientation of the columns and, therefore, the optical axis can be altered. Bright birefringence colors are observed after shearing the material in the columnar phase (photo A, plate 1). The **3,4-C$_n$** materials with $n = 10$ and $n = 12$ appear to melt directly from the room temperature phase to the isotropic phase; however, on cooling from the isotropic phase the materials go through a mesophase that could not be identified and then crystallize at a lower temperature (photo B, plate 1). No dendritic growths are observed on cooling from the isotropic, the optical axis is not normal to the glass plate (photo C, plate 1); the mesophase can be sheared if pressure is applied to the cover slip. This mesophase that does not appear to be a columnar phase is labeled X in Table 2.

All the **3,5-C$_n$** materials display a Col_h phase. The characteristic hexagonal nucleation evolving in the dendritic growth [14] was observed on cooling from the isotropic phase in all the **3,5-C$_n$** materials (photo D, plate 1). Except for **3,5-C$_8$**, a solid phase that cannot be sheared is observed on cooling from the Col_h phase. A rapidly growing crystallization nucleates at lower temperatures. The solid phase observed below the Col_h phase is labeled Cr_1 in Table 2. The Cr_1 phase is also observed in the DSC scans.

In the **3,4,5-C$_n$** materials, the columnar phase grows from the isotropic melt as a progressing front with dendrites (photo E, plate 1). No nucleations with hexagonal symmetry were observed; therefore, it is not possible to ascertain whether the columnar phase is rectangular or hexagonal. This columnar phase is labeled $Col_?$ in Table 2. The columns axes are well aligned perpendicular to the cell glass giving a clear conoscopic figure (photo F, plate 1). The fact that the material with three alkoxy chains does not display hexagonal nucleation, when the columnar phase grows from the isotropic melt indicates that this complex has significantly different surface tension anisotropy than the complexes with only two alkoxy chains [16–19].

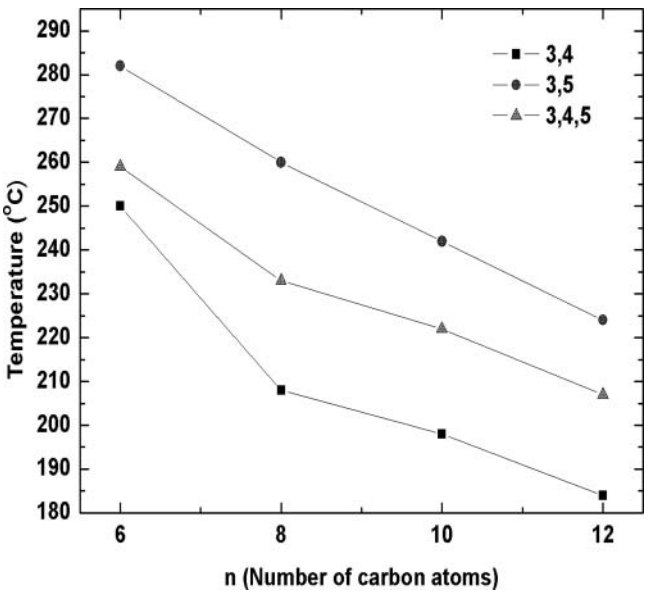


Figure 2. The clearing temperatures of the materials against chain length.

The clearing temperatures of the materials as a function of the alkoxy chain-length are plotted in Fig. 2. It can be seen that as is expected, increasing the chain length reduces the clearing temperature in all cases. The **3,4-C$_n$** materials have the lowest clearing temperatures and the **3,5-C$_n$** have the highest. The fact the clearing temperature of the **3,4,5-C$_n$** analogues is between that of the **3,4-C$_n$** and the **3,5-C$_n$** isomers is somehow unexpected. The unusual behavior together with the surface tension anisotropy of these tri-alkoxy analogues is the subject of further investigation.

Acknowledgments

The authors gratefully acknowledge research grants from the Third World Academy of Sciences (TWAS), Italy, the Ministry of Science and Technology, Bangladesh, and the financial support from Sultan Qaboos University, Sultanate of Oman.

References

[1] Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., & Vill, V. (1988). *Handbook of Liquid Crystals*, Wiley-VCH: Weinheim, Vols. 1–3.
[2] Collings, P. J., & Hird, M. (1997). *Introduction to Liquid Crystals*, Taylor & Francis: London.
[3] Li, W. R., Kao, K. C., Yo, Y. C., & Lai, C. K. (1999). *Helv. Chim Acta*, *82*, 1400–1407.
[4] Lai, C. K., Ke, Y. C., Su, J. C., & Li, W. R. (2002). *Liq. Crys.*, *29*, 915–920.
[5] Chien, C. W., Liu, K. T., & Lai, C. K. (2004). *Liq. Crys.*, *31*, 1007–1017.
[6] Chandrasekhar, S., Sadashiva, B. K., & Suresh, K. A. (1977). *Pramana J. Phys.*, *9*, 471.
[7] Foucher, P., Destrade, C., Tinh, N. H., Malthete, J., & Levelut, A. M. (1984). *Mol. Cryst. Liq. Cryst.*, *108*, 219.
[8] Tinh, N. H., Gasproux, C., & Destrade, C. (1981). *Mol. Cryst. Liq. Cryst.*, *68*, 101.
[9] Markovitsi, D. (2003). *Mol. Cryst. Liq. Cryst.*, *89*, 397.
[10] Ohta, K., Hatsusaka, K., Sugibayashi, M., Ariyoshi, M., Ban, K., Maeda, F., Naito, R., Nishizawa, K., Craats, A. M., &Warman, J. M. (2003). *Mol. Cryst. Liq. Cryst.*, *25*, 397.
[11] Lai, C. K., Tsai, C. H., & Pang, Y. S. (1998). *J. Mater. Chem.*, *8*(6), 1355.
[12] Abser, M. N., Bellwood, M., Buckley, C. M., Holmes, M. C., & McCabe, R. W. (1994). *J. Mater. Chem.*, *4*(8), 1173.
[13] Abser, M. N., Bellwood, M., Holmes, M. C., & McCabe, R. W. (1993). *J. Chem. Soc., Chem. Comm.*, *4*, 1062.
[14] Livolant, F., & Leforestier, A. (2000). *Biophys. J.*, *78*, 2716.
[15] Oswald, P. (1988). *J. Phys. France*, *49*, 1083.
[16] Kessler, D. A., & Levine, H. (1987). *Europhys. Lett.*, *4*, 215.
[17] Saito, Y., Goldbeck-Wood, G., & Mullerkrumbhaar, H. (1987). *Phys. Rev. Lett.*, *58*, 1541.
[18] Barbieri, A., Hong, D. C., & Langer, J. S. (1987). *Phys. Rev. A*, *35*, 1802.
[19] Glicksman, M. E. (1984). *Mat. Sci. Eng.*, *65*, 45.