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Bachcha Singh[a]; Ashwini Pandey[a]
[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India

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Liquid-Crystalline Properties of 2,5-Bis(4-n-Alkoxybenzoyloxy)-3,6-Dichloro-1,4-Benzoquinones and Their Copper (II) Complexes—Synthesis and Characterization

BACHCHA SINGH AND ASHWINI PANDEY

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India

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A new series of 2,5-bis(4-n-alkoxybenzoyloxy)-3,6-dichloro-1,4-benzoquinones, $C_6Cl_2O_2(OOCC_6H_4OR)_2$ and their copper (II) compounds, $C_6Cl_2O_2(OOC\text{-}C_6H_4OR)_2$ $Cu(CH_3COO)_2 \cdot H_2O$ where $R=C_mH_{2m+1}$ and $m=6,7,8,9,10,11,12,14$, and 16 have been synthesized. The compounds have been characterized by elemental analyses, fourier transform infrared (FTIR) far IR, ^1H, and ^{13}C NMR spectra. The UV-Visible, electron spin resonance (ESR), and magnetic susceptibility studies of the copper compounds have also been made. Mesomorphic properties of these compounds were studied by differential scanning calorimetry and polarizing microscopy. The mesomorphic nature of these compounds depends on the alkoxy chain length. The compounds ($m=6$, 7, 8, 14) exhibit the nematic mesophase. Compound ($m=9$)shows a nematic mesophase in heating cycle and both a nematic and a smectic A mesophase in the cooling cycle, whereas compound ($m=10$) shows enantiotropic nematic and smectic A mesophases. Compound ($m=11$) shows a monotropic smectic A mesophase and compound ($m=12$) shows an enantiotropic smectic A mesophase, whereas $m=16$ nonmesomorphic. The copper (II) complexes of these compounds were found to be nonmesogenic.

Keywords Chloranil based mesogens; copper (II) compounds; monotropic mesogens; nematic mesophase; smectic mesophase

Introduction

Liquid-crystalline materials are excellent examples of designed supermolecular materials and the cooperative physical properties of these materials have led to numerous technological applications [1]. Liquid crystals are useful materials for applications in passive block filters, laser-addressed devices, polarizers based on dichroic effects or thermochromism [2], thermometers (fever indicators, gadgets, design application, etc.), or warning signals (on heaters) and organic light-emitting diodes (OLEDS) [3]. Further, active matrix liquid crystals (AMLC) have been applied to various kinds of displays such as PC monitors, cellular phones and televisions [4,5]. Deformed helix liquid-crystal systems are also potential candidates to

Address correspondence to Bachcha Singh, Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India. E-mail: bsinghbhu@rediffmail.com

be used as reliable new generation memory devices [6], reflective-type liquid-crystal display (LCD) spatial light modulators, film reflectors, polarizers, field effect transistors, and sensors [7,8].

The organic liquid-crystalline species whose rigid core is benzoquinone are interesting systems from the point of view of electron transfer reactions, which play an important role in biological systems [9–12]. They may have interesting properties as possible agents for oxidations in the liquid-crystalline state, liquid-crystalline-charge transfer complexes, and liquid-crystalline conductors [13,14].

Chandrasekhar *et al.* [15] and Chadrasekhar [16] were the first to report unstable discotic mesomorph 2,3,5,6-tetrakis(octanoyloxy)-1,4-benzoquinone. Lillya and Thakur [17] reinvestigated and concluded that both the tetrakis heptanoyloxy- and octanoyloxy-1,4-benzoquinone **A** exhibit a columnar mesophase with a narrow temperature range. Matsutani *et al.* [18] synthesized three series of 2,3,5,6-tetrakis(4-alkoxybenzoyloxy)-1,4-benzoquinones **B**, 2,3,5,6-tetraalkoxy-1,4-benzoquinones **C**, 2,3,5,6-tetrakis(alkanoyl amino)-1,4-benzoquinones **D** and examined their mesomorphic properties. The benzoates **B** exhibits a simple crystal-isotropic liquid transition, suggesting that the aromatic ring of benzoate **B** was not suitable for improving coplanarity and rigidity of the 1,4-benzoquinone central core. They also obtained ethers **C** that showed two endothermic peaks at 32°C and 55°C, and a vague texture was reported in the above temperature range. The strengthening of the intermolecular interaction was achieved by substitution of an ester group of **A** by an amide group **D**, which displayed a dendritic texture after being cooled from the isotropic liquid. The mesophase was concluded as hexagonal columnar on the basis of reported optical texture.

Berg *et al.* (13) reported the synthesis of 2,5-dibenzoyloxy-3,6-dihydroxy-1,4-benzoquinone derivatives, their reduction products, and centrosymmetric tetraesters. The derivatives with short alkoxy groups ($n = 1$–5) showed only typical nematic Schlieren textures and droplets at the clearing point. The derivatives with long dodecyloxy groups exhibited an additional smectic phase (S_c or S_a).

A systematic study on the synthesis, characterization, and mesomorphic properties of hitherto uninvestigated compounds derived from 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) and their copper (II) complexes have been undertaken and results are reported here.

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Experimental

The Chemicals 4-Hydroxybenzoic Acid (Aldrich, Germany), Chloranil (Himedia, India), 1-Bromoalkanes (Aldrich, Germany) and Copper (II) Acetate Monohydrate (Aldrich, Germany), were used as supplied.

Techniques

Elemental analyses were performed on CE-440 Exeter Analytical CHN analyzer (USA). IR spectra (4000–100 cm^{-1}) were recorded on a Varian 3100 FT-IR Excalibur spectrophotometer (USA). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained by using a JEOL FT NMR AL 300 MHz spectrometer (Japan) using tetramethylsilane as internal standard. Electronic spectra were recorded on a UV-1700 Pharma spec Shimadzu UV-Visible spectrophotometer (Japan). Room temperature magnetic susceptibility measurements were performed on a Cahn-Faraday balance (USA) using $Hg[Co(NSC)_4]$ as standard. The magnetic susceptibility

was corrected for diamagnetism using Pascal's constants. Differential scanning calorimetry (DSC) thermograms were recorded by a Mettler Toledo TC 15 TA differential scanning calorimeter (Switzerland) at the rate of 10.0 K min^{-1} under nitrogen atmosphere using spec-pure-grade indium as standard by taking samples in closed lid aluminum pans. The transition temperatures from DSC have been determined with accuracy of ±0.1 K. The mesophase type was assigned by visual comparison with known phase standards using an HT 30.01 NTT 268 LOMO polarizing optical microscope (USA) fitted with a hot stage with temperature controlling accuracy of 0.1 K. Details of experimental techniques have been described elsewhere [19,20]. The copper content in the complexes was determined using an atomic absorption spectrophotometer (ASH Corp., USA).

Synthesis of Compounds

Potassium 4-n-hexyloxybenzoate **2** was prepared by alkylating 4-hydroxybenzoic acid **1** with 1-bromohexane in ethanol in the presence of KOH as described elsewhere [21]. All other homologous members of the series were prepared following the same procedure.

The compound 2,5-bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone **3** was prepared by reaction of potassium 4-n-hexyloxybenzoate **2** with chloranil in ethanol. The reaction mixture was stirred at 25°C for 8 h and then at 40°C for 30 min. The solution became dark brown and was filtered. The filtrate was evaporated under reduced pressure, resulting in an orange-colored residue. It was washed with distilled water, dried and recrystallized from chloroform. All other homologues of the series were prepared in a similar manner. The yield, NMR, IR data, and elemental analyses for the compounds are summarized as follows.

2,5-Bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{32}H_{34}Cl_2O_8$ (3a). Yield :72%. IR (KBr, cm^{-1}): 2936, 2864 (aliphatic C−H), 1680 (C=O, quinone), 1601 (Ph), 1578 (C=C, quinone), 1296 (OPh), and 773 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.06–8.03 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.85–1.34 (m, 16H, $-[CH_2]_n$), 0.91 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 171.9, 163.6, 132.3, 121.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 70.8, 68.2, 31.5, 29.0, 25.6, 22.5, 15.7, 13.9 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 417$, 256 nm. Elemental analyses: calculated for $C_{32}H_{34}Cl_2O_8$(%), C, 62.24; H, 5.54; found, C, 62.21; H, 5.42.

2,5-Bis(4-n-heptyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{34}H_{38}Cl_2O_8$ (3b). Yield: 70%. IR (KBr, cm^{-1}): 2929, 2850 (aliphatic C−H), 1678 (C=O, quinone), 1604 (Ph), 1576 (C=C, quinone), 1302 (OPh) and 773 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.05–8.03 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.80–1.25 (m, 20H, $-[CH_2]_n$), 0.89 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 172.1, 163.6, 132.3, 121.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 70.7, 68.2, 31.7, 29.0, 28.9, 25.9, 22.5, 15.7, 14.0 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 413$, 293, 255 nm. Elemental analyses: calculated for $C_{34}H_{38}Cl_2O_8$ (%), C, 63.25, H, 5.93; found, C, 63.18; H, 5.38.

2,5-Bis(4-n-octyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{36}H_{42}Cl_2O_8$ (3c). Yield: 72%. IR (KBr, cm^{-1}) : 2928, 2852 (aliphatic C−H), 1685 (C=O, quinone), 1608 (Ph), 1577 (C=C, quinone), 1296 (OPh), and 771 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.05–8.02 (d, 4H, ArH), 6.93–6.91 (d, 4H, ArH), 4.04–4.00

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(t, 4H, $-OCH_2$), 1.85–1.29 (m, 24H, $-[CH_2]_n$), 0.91 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 163.6, 132.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 68.2, 31.7, 29.3, 29.2, 29.0, 25.9, 22.6, 14.0 (CH_3). UV-visible (EtOH): $\lambda_{max} = 415$, 296, 260 nm. Elemental analyses: calculated for $C_{36}H_{42}Cl_2O_8$ (%), C, 64.18; H, 6.28; found, C, 64.42; H, 6.60.

2,5-Bis(4-n-nonyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{38}H_{46}Cl_2O_8$ (3d). Yield: 68%. IR (KBr, cm^{-1}): 2919, 2850 (aliphatic C−H), 1682 (C=O, quinone), 1606 (Ph), 1578 (C=C, quinone), 1307 (OPh), and 771 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.06–8.03 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.83–1.28 (m, 28H,$-[CH_2]_n$), 0.90 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 170.9, 162.6, 151.9, 137.6, 131.6, 131.3, 120.3, 113.1, 76.4, 76.2, 76.1, 76.0 ($CDCl_3$), 70.3, 70.1, 69.7, 30.8, 28.4, 28.0, 24.9, 21.6, 14.9 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 411$, 301, 253 nm. Elemental analyses: calculated for $C_{38}H_{46}Cl_2O_8$ (%), C, 65.04; H, 6.60; found, C, 65.32; H, 6.54.

2,5-Bis(4-n-decyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{40}H_{50}Cl_2O_8$ (3e). Yield: 65%. IR (KBr, cm^{-1}): 2926, 2854 (aliphatic C−H), 1680 (C=O, quinone), 1608 (Ph), 1578 (C=C, quinone), 1294 (OPh), and 773 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.06–8.03 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.82–1.27 (m, 32H, $-[CH_2]_n$), 0.90 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$) : 175.2, 171.7, 163.6, 152.9, 132.3, 131.4, 121.3, 114.1, 114.0, 77.4, 77.0, 76.5 ($CDCl_3$), 71.1, 70.7, 68.2, 64.8, 57.4, 31.8, 29.5, 29.3, 29.2, 29.0, 28.7, 26.0, 25.9, 22.6, 15.8, 14.0 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 413$, 310, 274, 243 nm. Elemental analyses: calculated for $C_{40}H_{50}Cl_2O_8$ (%), C, 65.83; H, 6.90; found, C, 65.28; H, 7.34.

2,5-Bis(4-n-undecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{42}H_{54}Cl_2O_8$ (3f). Yield: 69%. IR (KBr, cm^{-1}): 2923, 2855 (aliphatic C−H), 1680 (C=O, quinone), 1606 (Ph), 1576 (C=C, quinone), 1301 (OPh), and 776 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.04–8.01 (d, 4H, ArH), 6.93–6.90 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.80–1.25 (m, 36H, $-[CH_2]_n$), 0.88 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$) : 171.7, 163.6, 154.0, 138.6, 132.2, 131.7, 125.7, 121.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 71.3, 71.3, 71.1, 70.7, 68.2, 31.8, 29.5, 29.2, 25.9, 22.6, 15.8, 15.7, 14.0 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 418$, 309, 290, 254, 218 nm. Elemental analyses: calculated for $C_{42}H_{54}Cl_2O_8$ (%), C, 66.57; H, 7.18; found, C, 66.01; H, 6.70.

2,5-Bis(4-n-dodecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{44}H_{58}Cl_2O_8$ (3g). Yield: 64%. IR (KBr, cm^{-1}): 2918, 2850 (aliphatic C−H), 1682 (C=O, quinone), 1604 (Ph), 1578 (C=C, quinone), 1298 (OPh), and 796 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.04–8.01 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.82–1.26 (m, 40H,$-[CH_2]_n$), 0.88 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 171.8, 163.6, 132.3, 131.4, 121.3, 114.1, 114.0, 77.4, 77.0, 76.5 ($CDCl_3$), 71.3, 68.2, 68.1, 31.9, 29.6, 29.5, 25.9, 22.6, 15.8, 14.0 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 415$, 298, 277 nm. Elemental analyses: calculated for $C_{44}H_{58}Cl_2O_8$ (%), C, 67.25; H, 7.43; found, C, 67.14; H, 7.84.

2,5-Bis(4-n-tetradecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{48}H_{66}Cl_2O_8$ (3h). Yield: 67%. IR (KBr, cm^{-1}): 2920, 2851 (aliphatic C−H), 1677 (C=O, quinone), 1608 (Ph), 1577 (C=C, quinone), 1299 (OPh), and 800 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δ_H (ppm) : 8.04–8.02 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.82–1.26 (m, 48H, $-[CH_2]_n$), 0.90 (t, 6H, $-CH_3$). ^{13}C NMR δ_C

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($CDCl_3$): 171.1, 163.6, 132.3, 121.2, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 71.4, 71.1, 70.7, 68.2, 31.9, 29.6, 29.5, 25.9, 22.6, 15.9, 15.8, 14.1 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 417$, 310, 257 nm. Elemental analyses: calculated for $C_{48}H_{66}Cl_2O_8$ (%), C, 68.47; H, 7.90; found, C, 68.82; H, 7.54.

2,5-Bis(4-n-hexadecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, $C_{52}H_{74}Cl_2O_8$ (3i). Yield: 70%. IR (KBr, cm^{-1}): 2922, 2852 (aliphatic C−H), 1677 (C=O, quinone), 1606 (Ph), 1577 (C=C, quinone), 1296 (OPh), and 801 (C−Cl). ^1H NMR ($CDCl_3$, TMS) δH (ppm): 8.04–8.01 (d, 4H, ArH), 6.94–6.91 (d, 4H, ArH), 4.04–4.00 (t, 4H, $-OCH_2$), 1.82–1.25 (m, 56H, $-[CH_2]_n$), 0.90 (t, 6H, $-CH_3$). ^{13}C NMR δ_C ($CDCl_3$): 171.0, 163.6, 132.2, 114.1, 77.4, 77.2, 77.0, 76.5 ($CDCl_3$), 71.3, 71.1, 70.7, 68.2, 31.9, 29.8, 29.6, 25.9, 22.6, 15.9, 15.8, 14.1 (CH_3). UV-Visible (EtOH): $\lambda_{max} = 416$, 293, 254, 217 nm. Elemental analyses: calculated for $C_{52}H_{74}Cl_2O_8$ (%), C, 69.54; H, 8.30; Found, C, 69.92; H, 8.15.

Synthesis of Copper (II) Complex of 2,5-Bis(4-n-Hexyloxybenzoyloxy)-3,6-Dichloro-1-4-Benzoquinone (4)

A solution of 2,5-bis(4-n-hexyloxy benzoyloxy)-3,6-dichloro-1,4-benzoquinone (1.23 g, 2 mmol) in methanol (20 mL) and copper (II) acetate (0.39 g, 2 mmol) in methanol (20 mL) was mixed. The mixture was stirred at room temperature (25°C) for 1 h. The resulting light blue precipitate was filtered off and washed with methanol and dried under vacuum.

The copper (II) complexes of the remaining members of the homologous series were prepared adopting a similar method. These compounds were characterized as follows.

2,5-Bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{36}H_{42}Cl_2O_{13}Cu$ (4a). Yield: 82%. IR (KBr, cm^{-1}): 3561 (OH), 2933, 2863 (aliphatic C−H), 1679 (C=O, quinone), 1605 (Ph), 1549 ν_a(COO, acetate), 1409 ν_s (COO acetate), 1304 (C−O ester) 1249 (OPh), 773 (C−Cl), 465 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 551, 520, 473, 394, 329, 277, 205, 173, 149, 99 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 703$, 374, 318, 256, 224 nm. μ_{eff}: 1.73 BM. Elemental analyses: calculated for $C_{36}H_{42}Cl_2O_{13}Cu$ (%), C, 52.91; H, 5.18; Cu, 7.77; found, C, 52.72; H, 5.21; Cu, 7.62.

2,5-Bis(4-n-heptyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{38}H_{46}Cl_2O_{13}Cu$ (4b). Yield: 75%. IR (KBr, cm^{-1}): 3427 (OH), 2928, 2859 (aliphatic C−H), 1679 (C=O, quinone), 1606 (Ph), 1554 ν_a(COO acetate), 1405 ν_s (COO acetate), 1306 (C−O ester), 1253 (OPh), 783 (C−Cl), 465 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 568, 476, 309, 141 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 690$, 334, 309, 217 nm. μ_{eff}: 1.80 BM. Elemental analyses: calculated for $C_{38}H_{46}Cl_2O_{13}Cu$ (%), C, 53.99; H, 5.48; Cu, 7.51; found, C, 53.82; H, 5.42; Cu, 7.20.

2,5-Bis(4-n-octyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{40}H_{50}Cl_2O_{13}Cu$ (4c). Yield: 72%. IR (KBr, cm^{-1}): 3568 (OH), 2924, 2854, (aliphatic C−H), 1678 (C=O, quinone), 1593 (Ph), 1545 ν_a (COO acetate), 1431 ν_s(C−O acetate), 1299 (C−O ester), 1255 (OPh), 771 (C−Cl), 464 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 553, 503, 477, 390, 357, 324, 282, 231, 204, 156, 101 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 687$, 422, 267 nm. μ_{eff}: 1.83 BM. Elemental

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analyses: calculated for $C_{40}H_{50}Cl_2O_{13}Cu$ (%), C, 55.01; H, 5.77; Cu, 7.27; found, C, 55.12; H, 5.72; Cu, 7.12.

2,5-Bis(4-n-nonyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{42}H_{54}Cl_2O_{13}Cu$ (4d). Yield: 81%. IR (KBr, cm^{-1}): 3568 (OH), 2925, 2858, (aliphatic C−H), 1678 (C=O, quinone), 1601 (Ph), 1546 ν_a (COO acetate), 1427 ν_s (COO acetate), 1302 (C−O ester), 1254 (OPh), 776 (C−Cl), 466 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 552, 501, 473, 393, 360, 332, 294, 257, 205, 170, 110 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 666$, 476, 457, 244 nm. μ_{eff}: 1.85 BM. Elemental analyses: calculated for $C_{42}H_{54}Cl_2O_{13}Cu$ (%), C, 55.96; H, 6.03; Cu 7.05; found C, 55.58; H, 6.21; Cu 7.50.

2,5-Bis(4-n-decyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{44}H_{58}Cl_2O_{13}Cu$ (4e). Yield: 65%. IR (KBr, cm^{-1}): 3565 (OH), 2930, 2852 (aliphatic C−H), 1678 (C=O, quinone), 1605 (Ph), 1547 ν_a (COO acetate), 1430 ν_s (COO acetate), 1301 (C−O ester), 1252 (OPh), 773 (C−Cl), 468 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 468, 295, 188 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 668$, 301, 281 nm. μ_{eff}: 1.87 BM. Elemental analyses: calculated for $C_{44}H_{58}Cl_2O_{13}Cu$ (%), C, 56.86; H, 6.29; Cu, 6.83; found, C, 56.67; H, 6.52; Cu, 6.54.

2,5-Bis(4-n-undecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{46}H_{62}Cl_2O_{13}Cu$ (4f). Yield: 70%. IR (KBr, cm^{-1}): 3568 (OH), 2923, 2855 (aliphatic C−H), 1679 (C=O, quinone), 1608 (Ph), 1547 ν_a (COO acetate), 1433 ν_s (COO acetate), 1304 (C−O ester), 1254 (OPh), 798 (C−Cl), 467 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 555, 517, 474, 396, 327, 276, 205, 154 cm^{-1}. UV-Visible (nujol) : $\lambda_{max} = 670$, 424, 300 nm. μ_{eff}: 1.92 BM. Elemental analyses: calculated for $C_{46}H_{62}Cl_2O_{13}Cu$ (%), C, 57.70; H, 6.52; Cu, 6.63; found, C, 57.36; H, 6.25; Cu, 6.30.

2,5-Bis(4-n-dodecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{48}H_{64}Cl_2O_{12}Cu$ (4g). Yield: 72%. IR (KBr, cm^{-1}): 3568 (OH), 2923, 2854 (aliphatic C−H), 1677 (C=O, quinone), 1602 (Ph), 1548 ν_a (COO acetate), 1435 ν_s (COO acetate), 1301 (C−O ester), 1256 (OPh), 773 (C−Cl), 468 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 475, 386, 352, 323, 261, 205, 155 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 675$, 423, 380, 263, 220 nm. μ_{eff}: 2.01 BM. Elemental analyses: calculated for $C_{48}H_{66}Cl_2O_{13}Cu$ (%), C, 58.50; H, 6.75; Cu, 6.44; found, C, 58.27; H, 6.74; Cu, 6.18.

2,5-Bis(4-n-hexadecyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone monoaquacopper(II) acetate, $C_{56}H_{82}Cl_2O_{13}Cu$ (4i). Yield: 82%. IR (KBr, cm^{-1}): 3572 (OH), 2921, 2852, (aliphatic C−H), 1679 (C=O, quinone), 1601 (Ph), 1543 ν_a (COO acetate), 1437 ν_s (COO acetate), 1300 (C−O ester), 1255 (OPh), 771 (C−Cl), 470 (ρ_rCOO or $/\rho_{CH}$). Far IR (nujol): 477, 393, 355, 269, 227, 164, 94 cm^{-1}. UV-Visible (nujol): $\lambda_{max} = 691$, 413, 293 nm. μ_{eff}: 2.11 BM. Elemental analyses: calculated for $C_{56}H_{82}Cl_2O_{13}Cu$ (%), C, 61.27; H, 7.52; Cu, 5.78; found, C, 61.56; H, 7.58; Cu, 5.46.

Results and Discussion

The compounds 2,5-bis(4-n-alkoxybenzoyloxy)-3,6-dichloro-1,4-benzoquinones **3a-i** and their copper (II) complexes **4a-i** have been prepared as shown in Scheme 1. The elemental data are in agreement with the compounds formed. The IR and NMR spectral data are fully consistent with the structure. In the IR spectrum of **3a**, the

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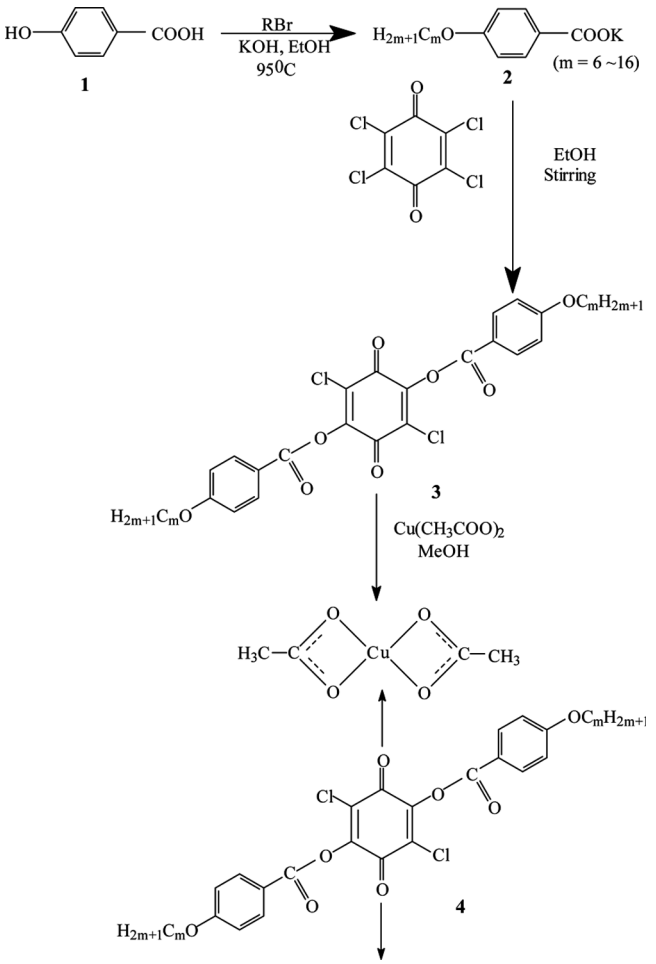
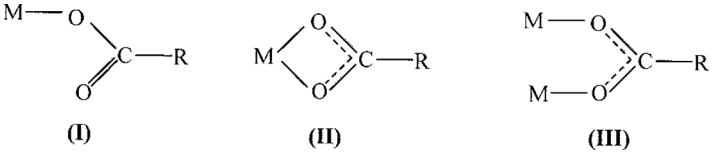


Scheme 1. Synthetic route for the compounds and their corresponding copper (II) complexes.

bands appearing at 2936, 2864, 1680, 1601 1578, 1296, and 773 cm^{-1} are attributed to ν(aliphatic C−H), ν(C=O) quinone, ring, ν(C=C) quinone ν(OPh), and ν(C−Cl) modes, respectively. Its ^{1}H NMR spectrum displays peaks at δ 8.06–8.03, 6.94–6.91, 4.02–4.00, 1.85–1.34, and 0.91, which are attributed to rings (first two peaks), $-OCH_2$, $-[CH_2]_n$ and $-CH_3$ protons, respectively. In the IR spectrum of the copper complex of 2,5-bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone **4a** splitting of (quinone) band occurs. One band is observed at lower frequency and an other one of low intensity is observed at almost similar frequency (1679 cm^{-1}). This suggests that only one quinone oxygen is bonded to the metal ion. The carboxylate ion may be bonded to a metal ion in the following three modes.



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The magnitude of difference $\Delta\nu$(COO) between the ν_a(COO) and ν_s(COO) frequency is used for distinction among the above three modes of bonding [22]. The asymmetric and symmetric stretching bands of carboxylate appear at 1549 and 1409 cm^{-1}. The value of $\Delta\nu$(COO) lying in the range 106–149 cm^{-1} for the chelating bidentate carboxylate suggests bonding of acetate in bidentate chelating manner. The far-IR spectrum of copper acetate monohydrate exhibits bands at 525, 480, 374, 330, 277, 233, 178, and 127 cm^{-1}. The compound 2,5-bis (4-n-hexyloxy benzoyloxy)-3,6-dichloro-1,4-benzoquinone **3a** shows bands at 322, 272, 210, and 129 cm^{-1}, respectively. The comparison of the far-IR spectra of the ligand and complex reveals the appearance of a new bands in the copper complex of 2,5-bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone **4a** at 551, 473, and 394 cm^{-1}, which are attributed to (Cu-O) of quinone, (Cu-O) of acetate moiety, and (Cu-O) of H_2O moiety, respectively, giving direct evidence of bonding between copper (II) and quinone. The electronic spectrum of chloranil exhibits bands at 408, 387, 337, 288, and 244 nm are due to $n-\pi^*$ and $\pi-\pi^*$ transitions. The spectrum of 2,5-bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone **3a** shows bands at 417 and 256 nm, which are assigned to $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively. The copper complex **4a** reveals bands at 703, 374, 318, 256, and 224 nm. A new broad band at 703 nm in the spectrum of the copper (II) complex may be assigned to an envelope of the dzx, $dxz \rightarrow dx^2 - y^2$, $dxy \rightarrow dx^2 - y^2$, and $dz^2 \rightarrow dx^2 - y^2$ transitions resulting from Jahn-Teller distortion. The remaining bands are assigned to π–π^* and n–π^* transitions of the ligand moiety. All the copper compounds exhibit magnetic moments in the range 1.73–2.11 BM, indicationg the presence of one unpaired electron, thereby suggesting that copper (II) acetate is monomeric.

The IR, NMR and electronic spectral data of the remaining ligands and their copper (II) complexes are explained and similar conclusions are drawn regarding the bonding of the ligands to the copper (II) and geometry of the resulting complexes. The copper (II) complexes were found to be insoluble in many solvents; therefore, crystals could not be developed and hence a single crystal study could not be pursued. The ESR spectrum of copper (II) complex of 2,5-bis(4-n-hexyloxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone **4a** is not resolved. It gives lines at 2940 G in parallel and at 3100 G in the perpendicular regions. These signals yield $g_{\|}$ (2.207) and $g_{\perp}$ (2.093). The higher value of $g_{\|}$ indicates distortion from octahedral geometry around Cu(II) and the presence of unpaired electron in $dx^2 - y^2$ orbital of the metal ion [23,24].

Optical Properties

The liquid-crystalline properties of 2,5-bis(4n-alkoxybenzoyloxy)-3,6-dichloro-1,4-benzoquinones **3a-i** and their copper (II) complexes **4** were investigated by polarizing optical microscope (POM) using a hot stage. The phase transition temperatures and enthalpies were measured by carrying out DSC thermal analysis. The phase transition temperatures and the corresponding enthalpy values for the compounds **3a-i** and their copper (II) complexes **4a-i** are summarized in Tables 1 and 2, respectively. The symbols K, SmA, N, and I are used to denote crystalline, smectic A, nematic, and isotropic phases, respectively. Compound **3b** exhibits endothermic peaks in heating cycle at 71.1°C, 87.3°C, and 104.9°C with enthalpies 5.14, 42.80, and 0.40 $kJmol^{-1}$, which define crystal (K^1) to crystal (K^2) phase, crystal (K^2) to mesophase, and mesophase to isotropic phase transitions, respectively. The

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Table 1. Phase transition temperatures, enthalpies (ΔH), and entropies (ΔS) of 2,5-bis(4-n-alkoxybenzoyloxy)-3,6-dichloro-1,4-benzoquinones

Compound	Transitions	T (°C)	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
3a	K^1–K^2	65.0	0.72	2.13
	K^2–K^3	72.2	16.33	47.30
	K^3–I	100.8	33.25	88.95
	I–N	142.5	0.71	1.70
	N–K^3	102.0	0.50	1.33
	K^3–K	87.8	36.37	100.80
3b	K^1–K^2	71.1	5.14	14.93
	K^2–N	87.3	42.80	118.78
	N–I	104.9	0.40	1.05
	I–N	142.1	0.37	0.89
	N–K^2	101.6	0.64	1.70
	K^2–K^1	78.8	19.67	55.89
	K^1–K	65.9	29.02	85.61
3c	K–N	72.5	35.76	103.49
	N–I	94.0	5.94	16.18
	I–N	87.3	18.28	50.73
	N–K	41.4	14.24	45.28
3d	K–N	57.6	7.83	23.68
	N–I	85.8	7.10	19.78
	I–N	100.3	0.08	0.21
	N–SmA	71.4	11.0	31.93
	SmA–K	42.8	32.91	104.21
3e	K–SmA	64.7	0.39	1.15
	SmA–N	71.9	1.93	5.59
	N–I	105.2	1.07	2.82
	I–N	101.4	1.19	3.17
	N–SmA	64.8	5.85	17.31
	SmA-K	59.1	0.92	2.77
3f	K^1–K^2	38.6	0.64	2.05
	K^2–K^3	49.6	2.40	7.43
	K^3–K^4	64.3	0.11	0.32
	K^4–K^5	69.7	4.45	12.98
	K^5–I	77.5	5.91	16.86
	I–SmA	100.8	0.04	0.10
	SmA–K	68.5	22.40	65.57
3g	K^1–K^2	66.6	1.75	5.15
	K^2–SmA	72.1	3.28	9.50
	SmA–I	146.6	1.04	2.47
	I–SmA	64.1	3.75	11.12
	SmA–K^2	58.6	0.74	2.22
	K^2–K^1	45.2	14.76	46.38
3h	K^1–K^2	60.5	22.23	66.65
	K^2–I	92.4	36.42	99.66

(*Continued*)

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Table 1. Continued

Compound	Transitions	T (°C)	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
	I–N	79.6	5.46	15.48
	N–K^2	74.3	4.82	13.87
	K^2–K^1	61.8	12.50	37.32
3i	K^1–K^2	48.5	2.86	8.7
	K^2–K^3	73.2	5.87	16.7
	K^3–I	82.2	11.90	30.2
	I–K^3	100.1	0.56	1.50
	K^3–K^2	74.8	37.97	109.14

exothermic peaks in cooling cycle of this compound appear at 142.1°C, 101.6°C, 78.8°C, and 65.9°C having enthalpies 0.37, 0.64, 19.67, and 29.02 and entropies 0.89, 1.70, 55.89, and 85.61 J K^{-1} mol^{-1}, respectively, which define isotopic to mesophase and mesophase to crystal phase transitions, respectively. The crystal to mesophase transition involves more enthalpy compared to the mesophase to isotropic phase transition. A similar trend is also observed in the entropy. The texture of the mesophase observed for this compound under polarizing microscope is characteristic of the nematic mesophase. The nematic droplets observed in the heating and cooling cycles consist of the characteristic black stripes or black brushes emanating from the central nuclei. These stripes 2 and 4 in number formed by disclination lines are generally arising due to defects in the molecular orientational order. The nematic droplets at 87.3°C in the heating cycle with prominent Schlieren texture merge to form a film in which the radiating stripes are not so conspicuous (Fig. 1(a)) compared to that in the cooling cycle at 142.1°C. The joining of radiating arms of one nucleus (molecule) with the other nuclei in the nematic texture is clearly seen (Fig. 1(b)). Similar mesomorphic properties are observed for the compound **3c**. Compounds **3a** and **3h** exhibit similar mesomorphism exhibiting a nematic mesophase in the coolinng cycle only.

Compound **3e** shows endothermic peaks at 64.7°C, 71.9°C, and 105.2°C, which are due to transitions of crystal to SmA, SmA to nematic phase, and nematic to isotropic phase, respectively. The smectic A phase (Fig. 2) with a focal conic texture is transient and changes to a nematic phase with characteristic black brushes and then to an isotropic phase at 105.2°C. In the cooling cycle, the isotropic phase changes to a nematic phase at 101.4°C, which further transits to a stratified structure with well-defined interlayer spacing SmA mesophase with ordered hexagonal structure at 64.8°C and finally transitions to solid crystalline phase at 59.1°C. Thus, this compound exhibits an enantiotropic smectic A to nematic mesophase transition.

Compound **3d** shows crystal to nematic and nematic to isotropic transitions in the heating cycle. However, in the cooling cycle it shows a nematic to SmA to crystal phase transition. The phase transition temperatures and accompanying enthalpies and entropies are given in Table 1. Compound **3g** exhibits endothermic peaks at 66.6°C, 72.1°C, and 146.6°C, which define crystal to crystal, crystal to SmA, and SmA to isotropic phase transitions, respectively. The exothermic peaks appear at 64.1°C, 58.6°C, and 45.2°C and show a reversal of the phase sequence I → SmA → K^2 → K^1. Compound **3f** exhibits numerous endothermic peaks indicating crystal to

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Table 2. Phase transition temperatures, transition enthalpies (ΔH), and entropies (ΔS) of 2,5-bis(4-n-alkoxybenzoyloxy)-3,6-dichloro-1,4-benzoquinone, monoaqua copper (II) acetate complexes

Compound	Transitions	T (°C)	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
4a	K^1–K^2	64.9	2.72	8.04
	K^2–K^3	105.2	2.73	7.21
	K^3–K^4	146.4	2.11	4.58
	K^4–I	187.6	2.41	5.23
	I–K^4	183.5	1.67	3.65
	K^4–K^3	142.2	2.34	5.63
	K^3–K^2	101.4	3.36	8.97
	K^2–K^1	59.0	3.35	10.08
4b	K^1–K^2	64.2	0.25	0.74
	K^2–K^3	78.2	7.77	22.12
	K^3–K^4	105.9	1.59	4.19
	K^4–K^5	146.7	1.16	2.76
	K^5–K^6	186.5	0.61	1.32
	K^6–I	196.4	16.80	35.78
	I–K^6	182.6	1.31	2.87
	K^6–K^5	141.0	1.28	3.09
	K^5–K^4	101.4	5.17	13.80
	K^4–K	97.9	4.95	13.34
4c	K^1–K^2	64.9	2.77	8.19
	K^2–K^3	105.4	2.72	7.18
	K^3–K^4	146.3	2.84	6.77
	K^4–K^5	187.8	2.62	5.68
	K^5–I	229.9	2.25	4.47
	I–K^5	225.4	2.51	5.03
	K^5–K^4	183.5	2.07	4.53
	K^4–K^3	142.2	2.93	7.05
	K^3–K^2	101.4	3.99	10.65
	K^2–K^1	65.2	1.97	5.82
4d	K^1–K^2	35.1	1.99	6.45
	K^2–I	114.5	1.44	3.71
4e	K^1–K^2	64.9	1.42	4.20
	K^2–K^3	105.2	1.43	3.78
	K^3–K^4	146.1	1.45	3.34
	K^4–K^5	187.5	1.09	2.36
	K^5–K^6	229.6	1.06	2.10
	K^6–I	272.5	0.95	1.74
	I–K^6	268.6	1.89	3.48
	K^6–K^5	225.7	1.52	3.04
	K^5–K^4	183.5	1.31	2.86
	K^4–K^3	142.4	1.73	4.16
	K^3–K^2	101.4	2.36	6.30
	K^2–K^1	59.09	2.23	6.71

(*Continued*)

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Table 2. Continued

Compound	Transitions	T (°C)	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
4f	K^1–K^2	65.5	0.61	1.80
	K^2–K^3	92.3	6.36	17.40
	K^3–K^4	106.0	1.72	4.53
	K^4–K^5	194.5	90.52	193.72
	K^5–I	215.2	6.81	13.94
	I–K^5	181.9	0.14	0.30
	K^5–K^4	140.8	0.47	1.13
	K^4–K^3	109.1	11.48	30.04
	K^3–K	99.8	0.62	1.66
4g	K^1–K^2	64.9	2.77	8.19
	K^2–K^3	105.4	3.08	8.13
	K^3–K^4	146.3	2.56	6.10
	K^4–K^5	187.8	2.75	5.96
	K^5–I	229.9	2.15	4.27
	I–K^5	225.4	2.61	5.23
	K^5–K^4	183.5	2.21	4.84
	K^4–K^3	142.2	2.94	7.08
	K^3–K^2	101.4	3.61	9.64
	K^2–K^1	58.9	3.92	11.80
4i	K^1–K^2	117.3	16.57	42.44
	K^2–I	131.3	9.09	22.45
	I–K^2	113.6	17.08	44.16
	K^2–K^1	90.8	24.65	67.81

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crystal polymorphism and changes to an isotropic phase at 77.5°C. However, on cooling it goes from isotropic to SmA followed by crystallization. Thus, this compound has features of monotropic liquid crystallinity with the appearance of an SmA phase only in the cooling cycle. The origin of the smectic phase is the interlayer attractions, which are weak compared to the lateral forces between the molecules, and the layers are able to slide over one another relatively easily. This gives rise to fluid property to the system having higher viscosity than the nematic mesophase. The flexibility of layers leads to distortion accounting for the focal conic pattern of smectic A mesophase. Compound **3i** exhibits no mesomorphic behavior and only a crystal to isotropic phase transition is observed. The endothermic peaks appearing at 48.5°C, 73.2°C, and 82.2°C define the $K^1 \rightarrow K^2$, $K^2 \rightarrow K^3$, $K^3 \rightarrow I$ phase transitions respectively. A mosaic pattern is observed at 73.2°C but it does not define a mesophase. It has a tendency toward nematic phase. The exothermic peaks appearing at 100.1°C and 74.8°C define $I \rightarrow K^3$ and $K^3 \rightarrow K^2$ transitions, respectively.

The enantiotropic nematic mesophase for the compounds with $m = 6$, 7 and 8, enantiotropic nematic and Smetic A mesophases for $m = 9$ and 10, monotropic smectic A mesophase for $m = 11$, enantiotropic Smectic A mesophase for $m = 12$, and monotropic nematic mesophase for $m = 6$, 14 are inferred. The compound with $m = 16$ is nonmesogenic in nature.

(a)

(b)

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Figure 1. (a) Photomicrograph of the nematic Schlieren texture at 87.3°C of compound **3b** in the heating cycle. (b) Photomicrograph of the nematic Schlieren texture at 142.1°C of compound **3b** in the cooling cycle.

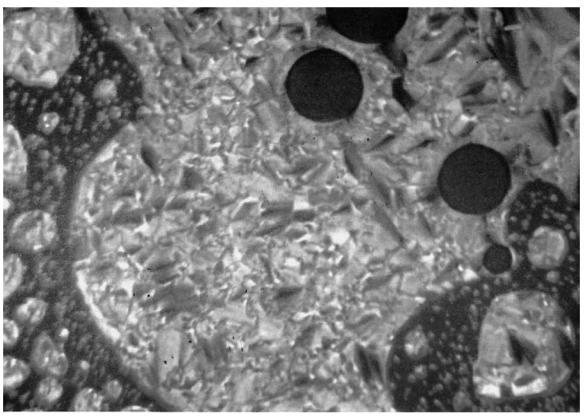

Figure 2. Photomicrograph of the smectic A phase at 64.7°C of compound **3e** in the heating cycle.

Conclusions

The following structure-mesophase relationship for this series of the compounds is inferred. As the alkoxy chain length increases, the nematic phase is first be stabilized (Mair Saupe theory) [25] until the smectic phase appears due to further association promoted by mutual interaction of the chains. The copper (II) complexes exhibit crystal to crystal and crystal to isotropic phase transitions in the heating cycle and subsequent crystal to crystal transitions in the cooling cycle with no mesomorphism. The nonmesogenic nature of the copper complexes may be due to strong hydrogen bonding between coordinated water molecule and the oxygen, which is sufficient to pack the molecules giving only solid-state properties.

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