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Liquid Crystalline Properties of 2,5-Bis[4-n-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones: Synthesis and Characterization

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A new series of 2,5-bis[4-n-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones, $C_6Cl_2O_2(OCOC_6H_4OCOC_6H_4OR)_2$, where $R = C_mH_{2m+1}$ and $m = 7$, 8, 9, 10, 11, 12, 14, and 16, have been synthesized. These compounds have been characterized by elemental analyses, FT-IR, UV-visible, ^1H, and ^{13}C NMR spectra. Mesomorphic properties of these compounds were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The mesomorphic nature of these compounds depends on the alkoxy chain length. The compounds ($m = 7$, 8, 9, 10) exhibit a monotropic nematic mesophase in cooling cycle, while the compounds ($m = 11$, 12, 14, and 16) show no mesogenic behavior in both heating and cooling cycles. The intermolecular interactions play a vital role in the mesogenic nature of these compounds. In higher homologues of the series the intermolecular interactions become more prominent leading to loss in mesogenic nature.

Keywords Differential scanning calorimetry; intermolecular interactions; monotropic nematic mesophase; polarizing optical microscopy

1. Introduction

Liquid crystalline materials may be used in passive block filters, laser addressed devices, polarizers based on dichroic effects, and devices based on thermochromism [1]. The organic liquid crystalline materials with benzoquinone rigid core are prone to electron transfer reactions which may play an important role in biological systems [2–5]. They may have an important role as oxidants in the liquid crystalline state, liquid crystalline charge transfer complexes, and liquid crystalline conductors [6,7]. The use of quinone functionality in the linkage unit of laterally bridged oligoporphyrin as a switch for controlling electronic coupling between the termini has been examined [8].

Nakasuji and Yamamoto [9] reported amphoteric redox nature of p-benzoquinone with donor and acceptor substituents. Primary, secondary, and tertiary amines

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both aliphatic and aromatic are shown to react with p-chloranil in dioxan/2-propanol [10]. Chandrasekhar et al. [11,12] were the first to report an unstable discotic mesophase of 2,3,5,6-tetrakis(octanoyloxy)-1,4-benzoquinone. Lillya and Thakur reinvestigated and concluded columnar mesophase with a narrow temperature range for both the tetrakis heptanoyloxy and octanoyloxy-1,4-benzoquinone **(1)**. Matsutani et al. [13] synthesized three series of 2,3,5,6-tetrakis(4-alkoxybenzoyloxy)-1,4-benoquinones **(2)**, 2,3,5,6-tetraalkoxy-1,4-benzo-quinones **(3)**, 2,3,5,6-tetrakis (alkanoylamino)-1,4-benzoquinones **(4)**, and examined their mesomorphic properties. The benzoates **2** exhibit a simple crystal-isotropic liquid transition, while the aliphatic esters **1** are mesogenic. Thus, it is concluded that the aromatic ring of benzoate **2** was not suitable for improving coplanarity and rigidity to the 1,4-benzoquinone central core. They also obtained ethers **3** that showed two endothermic peaks at 32°C and 55°C, and vague texture was reported in the above temperature range. The strengthening of the intermolecular interaction was achieved by substitution of an ester group of **1** by an amide group to yield **4** which displayed a dendric texture after being cooled from the isotropic liquid. The hexagonal columnar mesophase was reported on the basis of optical texture.

Berg et al. [6] reported 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 exhibit an additional smectic phase (S_C or S_A).

In view of the above observations, a systematic study on the synthesis, characterization and the mesomorphic properties of hitherto uninvestigated compounds derived from 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) have been undertaken. The results are communicated in the present article.

2. Experimental

Materials

4-Hydroxybenzoic acid, 1-bromoalkanes, potassium hydroxide, sodium bicarbonate (all Aldrich), thionyl chloride (Qualigens), and chloranil (Himedia) were used as obtained. All other reagents and solvents purchased commercially were used after further purification.

Techniques

Elemental analyses were performed on CE-440 Exeter Analytical CHN analyzer. IR spectra (4000–100 cm^{-1}) were recorded on Varian 3100 FT-IR Excalibur spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained by using a JEOL FT NMR AL 300 MHz spectrometer using tetramethyl silane as internal standard. Electronic spectra were recorded on UV-1700 Pharma Spec Shimadzu UV-Visible spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded on Mettler Toledo TC 15 TA differential scanning calorimeter at the rate of 10.0 K min^{-1} under nitrogen atmosphere using spec pure grade indium as standard by taking samples in close lid aluminum pans. The transition temperatures from DSC have been determined with accuracy of ±0.1 K. The mesophase identification was done by visual comparison with known phase standards using HT-30.01 NTT

268 LOMO polarizing optical microscope (POM) fitted with a hot stage and temperature controlling accuracy of 0.1 K.

Synthesis of Compounds

*Synthesis of 4-Heptyloxy Benzoic Acid (**2**).* To a solution of 4-hydroxybenzoic acid (1.18 g, 10 mmol) in dry ethanol (30 ml) and of KOH (1.68 g, 30 mmol) in dry ethanol (60 ml), 1-bromoheptane (1.57 ml, 10 mmol) was added dropwise with constant stirring. The reaction mixture was refluxed for ~14 h under dry atmosphere and allowed to cool to room temperature. The solid alkoxy potassium salt thus obtained was separated out by filtration under suction and treated with dilute HCl until the pH of the reaction mixture reached to ~2. The crude solid white product was filtered off, washed thoroughly with water, and recrystallized successively from glacial acetic acid and toluene. Yield: 72%, IR (KBr, cm^{-1}): 3423 (OH), 2929, 2852 (aliphatic C−H), 1685 (C=O), 1606, 1511 (Ph), 1305, 1256 (OPh). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 11.90 (s, 1 H, −OH), 8.06–8.03 (d, 2 H, ArH), 6.94–6.91 (d, 2 H, ArH), 4.04–4.00 (t, 2 H, $-OCH_2$), 1.83–1.31 (m, 10 H, $-[CH_2]_n$), 0.89–0.87 (t, 3 H, $-CH_3$).

All the homologous members of the series have been prepared using the above procedure (Scheme 1).

*Synthesis of 2,5-Bis[4-hydroxybenzoyloxy]-3,6-dichloro-1,4-benzoquinone (**3**).* An aqueous solution (40 ml) of $NaHCO_3$ (0.67 g, 8 mmol) was added to an ethanolic solution (20 ml) of 4-hydroxybenzoic acid (0.44 g, 8 mmol) till effervescence ceased. To this solution 2,3,5,6,-tetrachloro-1,4-benzoquinone (Chloranil) (0.98 g, 4 mmol) was added with stirring. The reaction mixture was stirred further for 6 h with heating at 40°C. A reddish brown precipitate appeared which was filtered, washed with water followed by ethanol and ether. The product was washed with toluene thrice (3 × 5 ml) to remove chloranil and dried under vacuum. Recrystallization of the compound from ethyl acetate afforded orange crystals in 72% yield. IR (KBr, cm^{-1}): 3449 (OH), 1768 (C=O ester), 1682 (C=O quinone), 1589 (C=C quinone), 1502 (Ph), 1294 (OPh), 765 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 12.94 (s, 2 H, −OH), 7.95 (d, 4 H, ArH), 7.36 (d, 4 H, ArH). ^{13}C NMR (DMSO) δ_c (ppm): 173.0, 166.5, 159.1, 150.0, 139.4, 131.4. 130.0, 126.3, 116.0, 40.3, 40.0, 39.7, 39.5, 39.2, 38.9, 38.6. Elemental analyses: calculated (for $C_{20}H_{10}Cl_2O_8$), C, 53.47; H, 2.24%, found, C, 53.12; H, 2.01%.

*Preparation of 2,5-Bis[4-n-heptyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{48}H_{46}Cl_2O_{12}$ (**4a**).* 4-Heptyloxybenzoic acid (1.88 g, 8 mmol) was dissolved in dry chloroform (50 ml), and thionyl chloride (0.65 ml, 9 mmol) was added and refluxed for 7 h. The solvent and excess thionyl chloride were removed under reduced pressure to give 4-heptyloxy benzoyl chloride as an yellow oil. The above acid chloride was treated with 2,5-bis[4-hydroxybenzoyloxy]-3,6-dichloro-1,4-benzoquinone **(3)** (1.79 g, 4 mmol) in dry dichloromethane (50 ml) containing 2–3 drops of pyridine. The reaction mixture was refluxed for 8 h with constant stirring. An orange color solution was obtained. The solvent was removed under reduced pressure to give oil. It was triturated with water (40 ml) and extracted with CH_2Cl_2(2 × 10 ml) and dried. Evaporation of the solvent followed by crystallization from chloroform yielded orange crystals. Yield: 73%, IR (KBr, cm^{-1}): 2923, 2853

(aliphatic C−H), 1770 (C=O ester), 1682 (C=O quninone), 1605, 1510 (Ph), 1310, 1256 (OPh), 764 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.08–8.01 (dd, 8 H, ArH), 6.99–6.90 (dd, 8 H, ArH), 4.06–3.99 (m, 4 H, $-OCH_2$), 1.80–1.27 (m, 20 H, $-[CH_2]_n$), 0.88–0.86 (t, 6 H, $-CH_3$). ^{13}C NMR (DMSO) δ_c (ppm): 172.1, 169.4, 166.4, 163.6, 162.8, 140.7, 132.2, 131.4. 131.0, 122.5, 121.7, 121.3, 114.5, 114.3, 113.9, 77.4, 77.0, 76.5 ($CDCl_3$), 68.2 ($-OCH_2$), 68.1, 60.5, 31.7, 29.0, 25.9, 22.5, 14.0 (CH_3). UV-visible (EtOH): $\lambda_{max} = 344$, 277 nm. Elemental analyses: calculated (for $C_{48}H_{46}Cl_2O_{12}$), C, 65.08; H, 5.23%, found, C, 64.93; H, 4.81%. All other homologous members of the series were prepared by the similar procedure. Their IR, NMR (^{1}H, ^{13}C) UV-visible and elemental data are summarized as follows.

*2,5-Bis[4-n-octyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{50}H_{50}Cl_2O_{12}$ (**4b**).* Yield: 71%. IR (KBr, cm^{-1}): 2928, 2853 (aliphatic C−H), 1775 (C=O ester), 1681 (C=O quinone), 1604, 1511 (Ph), 1306, 1256 (OPh), 766 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 7.90–7.85 (dd, 8 H, ArH), 7.03–6.97 (dd, 8 H, ArH), 4.04–4.00 (m, 4 H, $-OCH_2$), 1.74–1.27 (m, 24 H, $-[CH_2]_n$), 0.86 (t, 6 H, $-CH_3$). ^{13}C NMR ($CDCl_3$) δ_C (ppm): 171.9, 166.4, 163.6, 162.8, 132.4, 132.2, 131.4. 122.5, 121.3, 116.3, 114.1, 113.9, 77.4, 76.9, 76.5 ($CDCl_3$), 68.2 ($-OCH_2$), 68.1, 60.5, 31.7, 29.2, 29.1, 29.0, 25.9, 22.6, 14.0 (CH_3). UV-visible (EtOH): $\lambda_{max} = 276$, 251 nm. Elemental analyses: calculated (for $C_{50}H_{50}Cl_2O_{12}$), C, 65.71; H, 5.51%, found, C, 65.42; H, 5.93%.

*2,5-Bis[4-n-nonyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{52}H_{54}Cl_2O_{12}$ (**4c**).* Yield: 72%. IR (KBr, cm^{-1}): 2926, 2854 (aliphatic C−H), 1773 (C=O ester), 1682 (C = O quinone), 1605, 1512 (Ph), 1307, 1255 (OPh), 766(C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.08–8.04 (dd, 8 H, ArH), 6.95–6.87 (dd, 8 H, ArH), 4.06–4.00 (m, 4 H, $-OCH_2$), 1.83–1.28 (m, 28 H, $-[CH_2]_n$), 0.88–0.86 (t, 6 H, $-CH_3$). UV-visible (EtOH): $\lambda_{max} = 349$, 284, 268 nm. Elemental analyses: calculated (for $C_{52}H_{54}Cl_2O_{12}$), C, 66.31; H, 5.77%, found, C, 66.22; H, 5.34%.

*2,5-Bis[4-n-decyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{54}H_{58}Cl_2O_{12}$ (**4d**).* Yield: 76%. IR (KBr, cm^{-1}): 2923, 2852 (aliphatic C−H), 1775 (C = O ester), 1681 (C = O quinone), 1604, 1511 (Ph), 1306, 1256 (OPh), 770 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.06–8.03 (dd, 8 H, ArH), 6.94–6.91 (dd, 8 H, ArH), 4.04–4.00 (m, 4 H, $-OCH_2$), 1.83–1.27 (m, 32 H, $-[CH_2]_n$), 0.90–0.86 (t, 6 H, $-CH_3$). UV-visible (EtOH): $\lambda_{max} = 273$, 245, 217 nm. Elemental analyses: calculated (for $C_{54}H_{58}Cl_2O_{12}$), C, 66.86; H, 6.02%, found, C, 66.58; H, 6.31%.

*2,5-Bis[4-n-undecyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{56}H_{62}Cl_2O_{12}$ (**4e**).* Yield: 75%. IR (KBr, cm^{-1}): 2931, 2855 (aliphatic C−H), 1773 (C = O ester), 1684 (C = O quinone), 1605, 1511 (Ph), 1307, 1256 (OPh), 770 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.05–7.96 (dd, 8 H, ArH), 6.93–6.87 (dd, 8 H, ArH), 4.04–3.97 (m, 4 H, $-OCH_2$), 1.80–1.27 (m, 36 H, $-[CH_2]_n$), 0.91–0.87 (t, 6 H, $-CH_3$). UV-visible (EtOH): $\lambda_{max} = 342$, 274 nm. Elemental analyses: calculated (for $C_{56}H_{62}Cl_2O_{12}$), C, 67.39; H, 6.26%, found, C, 67.54; H, 6.42%.

*2,5-Bis[4-n-dodecyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{58}H_{66}Cl_2O_{12}$ (**4f**).* Yield: 68%. IR (KBr, cm^{-1}): 2925, 2851 (aliphatic C−H), 1775 (C=O ester), 1681 (C=O quinone), 1605, 1510 (Ph), 1307, 1257 (OPh), 770 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.05–7.96 (dd, 8 H, ArH), 6.93–6.87 (dd, 8 H, ArH), 4.04–3.97 (m, 4 H, OCH_2), 1.80–1.31 (m, 40 H, $-[CH_2]_n$), 0.91–0.87 (t, 6 H,

$-CH_3$). UV-visible (EtOH): $\lambda_{max} = 293$, 271 nm. Elemental analyses: calculated (for $C_{58}H_{66}Cl_2O_{12}$), C, 67.89; H, 6.48%, found, C, 67.62; H, 6.27%.

*2,5-Bis[4-n-tetradecyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{62}H_{74}Cl_2O_{12}$ (**4g**).* Yield: 74%. IR (KBr, cm^{-1}): 2924, 2854 (aliphatic C−H), 1781 (C=O ester), 1683 (C=O quinone), 1605, 1510 (Ph), 1310, 1258 (OPh), 765 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.06–7.82 (dd, 8 H, ArH), 7.10–6.95 (dd, 8 H, ArH), 4.04–3.97 (m, 4 H, $-OCH_2$), 1.70–1.21 (m, 48 H, $-[CH_2]_n$), 0.91–0.82 (t, 6 H, $-CH_3$). UV-visible (EtOH): $\lambda_{max} = 302$, 268 nm. Elemental analyses: calculated (for $C_{62}H_{74}Cl_2O_{12}$), C, 68.81; H, 6.89%, found, C, 68.76; H, 6.82%.

*2,5-Bis[4-n-hexadecyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone, $C_{66}H_{82}Cl_2O_{12}$ (**4h**).* Yield: 70%. IR (KBr, cm^{-1}): 2919, 2852 (aliphatic C−H), 1775 (C=O ester), 1682 (C=O quinone), 1605, 1511 (Ph), 1307, 1283 (OPh), 766 (C−Cl). ^{1}H NMR ($CDCl_3$, TMS) δ_H (ppm): 8.11–7.96 (dd, 8 H, ArH), 6.90–6.87 (dd, 8 H, ArH), 4.04–3.97 (m, 4 H, $-OCH_2$), 1.80–1.25 (m, 56 H, $-[CH_2]_n$), 0.90–0.85 (t, 6 H, $-CH_3$). UV-visible (EtOH): $\lambda_{max} = 341$, 277 nm. Elemental analyses: calculated (for $C_{66}H_{82}Cl_2O_{12}$), C, 69.64; H, 7.26%, found, C, 69.52; H, 7.12%.

3. Results and Discussion

The compound 2,5-bis[4-hydroxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone **3** exhibits IR absorption bands at 3449 (OH), 1768 (C=O ester), 1682 (C=O quinone), 1589 (C=O quinone), 1502 (Ph), 1294 (OPh), and 765 (C−Cl) cm^{-1}. The compound 2,5-bis[4-n-heptyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone **4a** displays IR spectral bands at 2923, 2853 (aliphatic C−H), 1770 (C=O ester), 1682 (C=O quinone), 1605, 1510 (Ph), 1310, 1256 (OPh), and 764 (C−Cl) cm^{-1}. The disappearance of ν(OH) band and appearance of a band centered at 1770 cm^{-1} due to phenyl ester moiety in the compound **4a** confirms its structure. Proton NMR spectrum of the compound 2,5-bis[4-hydroxybenzoyloxy]-3,6-dichloro-1,4-benzoquinone exhibits signals at δ 12.94 (s, 2H, OH) and 7.95 (d, 4H, ArH), 7.36 (d, 4H, ArH) ppm. The compound 2,5-bis[4-n-heptyloxy benzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone **4a** exhibits NMR signals at δ 8.08–8.01 (dd, 8 H, ArH), 6.99–6.90 (dd, 8 H, ArH), 4.06–3.99 (m, 4 H, $-OCH_2$), 1.80–1.27 (m, 20 H, $-[CH_2]_n$), and 0.88–0.86 (t, 6 H, $-CH_3$) ppm. Thus the disappearance of δ OH and the appearance of additional signal of aromatic ring in the compound **4a** confirms the formation of this compound as inferred from IR spectra also. The chain length has no significant effect on the position of the signals due to $-OCH_2$, $-[CH_2]_n$, and CH_3 protons, respectively. The UV-visible spectrum of compound 2,5-bis[4-n-heptyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone **4a** exhibits UV bands at 344 and 277 nm which are assigned as $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ transitions.

4. Optical Properties

The liquid crystalline properties of 2,5-bis[4-n-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones **4a–i** were investigated by POM using a hot stage. The phase transition temperatures and enthalpies were measured by carrying out DSC thermal analysis. The phase transition temperatures along with the enthalpy values for the compounds are summarized in Table 1. The symbols K, N, and I

Table 1. Thermal transition temperatures, associated enthalpy (ΔH), and entropy (ΔS) changes of 2,5-bis[4-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones

Compound	Transitions	T/°C	ΔH/kJmol^{-1}	ΔS/JK^{-1}mol^{-1}
4a	K^1–I	86.4	81.94	227.99
	I–N	80.5	23.99	67.86
	N–K^1	64.1	34.32	101.80
	K^1–K	47.5	8.22	25.64
4b	K^1–K^2	64.2	0.22	0.65
	K^2–K^3	71.4	17.04	49.47
	K^3–K^4	84.3	8.29	23.20
	K^4–K^5	104.6	0.08	0.21
	K^5–I	220.0	0.06	0.12
	I–N	150.5	0.11	0.25
	N–K^5	109.7	0.15	0.39
	K^5–K	83.3	16.04	45.01
4c	K^1–K^2	64.4	0.12	0.35
	K^2–K^3	79.3	16.82	47.74
	K^3–K^4	104.6	0.10	0.26
	K^4–K^5	145.4	0.17	0.40
	K^5–I	186.9	0.07	0.15
	I–N	150.7	0.25	0.59
	N–K^5	109.7	0.24	0.62
	K^5–K^4	55.2	5.11	15.56
	K^4–K	39.5	19.99	63.96
4d	K^1–K^2	64.8	0.73	2.16
	K^2–K^3	84.4	18.25	51.06
	K^3–K^4	90.2	8.26	22.74
	K^4–K^5	104.9	0.42	1.11
	K^5–K^6	145.8	0.45	1.07
	K^6–I	187.1	0.41	0.89
	I–N	150.5	1.13	2.66
	N–K^6	109.5	4.01	10.48
	K^6–K^5	102	4.19	11.17
	K^5–K^4	87.7	18.05	50.04
	K^4–K	63.6	15.79	46.91
4e	K–I	91.3	55.98	153.66
	I–K	69.0	24.95	72.95
4f	K^1–K^2	64.6	0.15	0.44
	K^2–K^3	77.4	2.67	7.61
	K^3–K^4	84.0	5.56	15.57
	K^4–I	192.0	0.06	0.12
	I–K^4	150.5	0.16	0.37
	K^4–K^3	109.4	0.42	1.09
	K^3–K^2	98.1	1.47	3.96
	K^2–K^1	81.1	3.57	10.08
	K^1–K	67.1	3.84	11.29

(*Continued*)

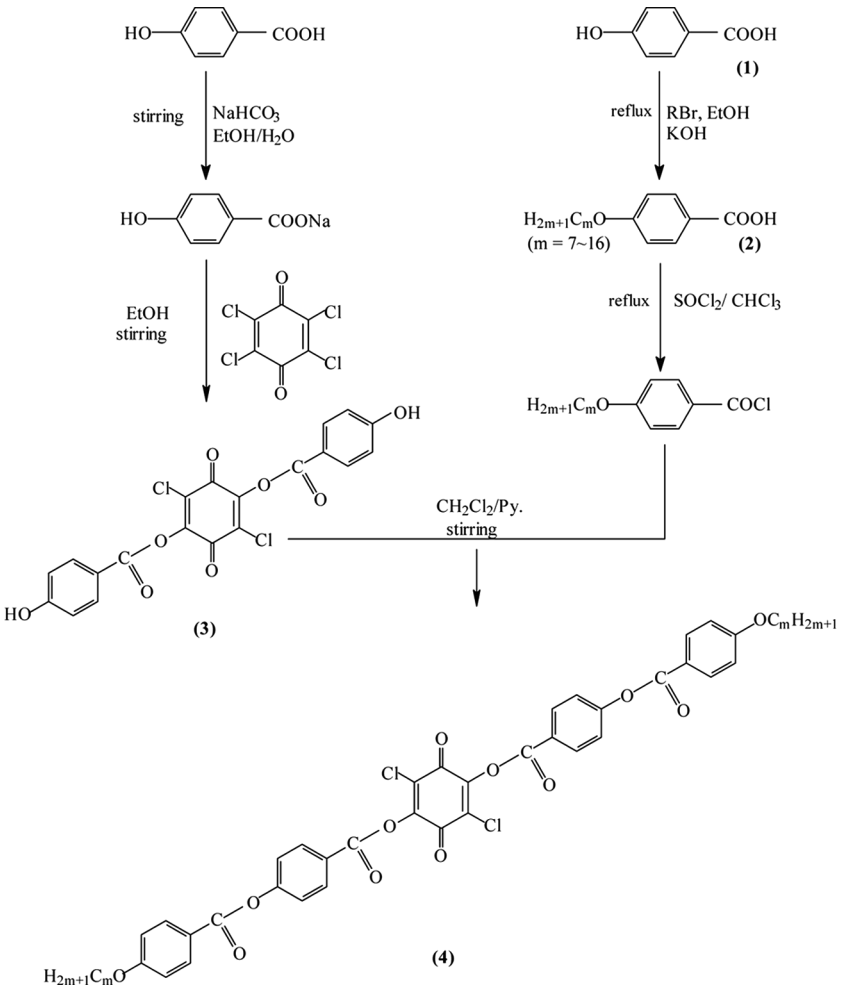
Table 1. Continued

Compound	Transitions	T/°C	$\Delta H/kJmol^{-1}$	$\Delta S/JK^{-1}mol^{-1}$
4g	K–I	67.6	20.14	59.13
	I–K	62.6	17.74	52.86
4h	K^1–K^2	44.6	12.38	38.97
	K^2–K^3	73.1	71.25	205.86
	K^3–I	192.2	0.04	0.08
	I–K^3	150.7	0.11	0.25
	K^3–K^2	109.6	0.20	0.52
	K^2–K^1	60.8	0.67	2.00
	K^1–K	49.2	67.44	209.31

are used to denote crystalline, nematic, and isotropic phases, respectively. The compound 2,5-bis[4-n-heptyloxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinone **4a** exhibits an endothermic peak at 86.4°C ($\Delta H = 81.94\,kJmol^{-1}$) due to the crystal-to-isotropic transition. Three exothermic peaks are observed at 80.5°C ($\Delta H = 23.99\,kJmol^{-1}$), 64.1°C ($\Delta H = 34.32\,kJmol^{-1}$), and 47.5°C ($\Delta H = 8.22\,kJmol^{-1}$) showing transitions from the isotropic-to-mesophase, mesophase-to-crystal, followed by another crystal phase. The texture of the mesophase observed under polarizing microscope is characterized by the appearance of numerous dense nematic bubbles (droplets) which possess disclination (defects) invariably within them. These disclinations seen within the radial structure are hedgehog defects giving rise to schlieren texture with characteristic black brushes 2–4 in numbers. The disclination within the nematic droplets observed in cooling cycle are arising as the elastic energy density of a nematic molecule is sufficiently large, and the orientation of the nematic director becomes indistinct. These disclinations are high energy structures and the nematic ordering adopts a configuration which minimizes both the number and strength of these defects. The changes in the nematic alignment (due to applied field, changes in temperature, etc.) can force a disclination of one type to transform into another form but these studies have not been performed in our case. A closer look reveals that the brushes come together in a singular point and are four-fold. The singularities are topological defects which are assigned certain strength. The molecule shows (+ve) defects with the rotation of four-fold brushes in the same direction. The defect-free sample area is also seen indicating that the defects are of same strengths and can annihilate.

The compound **4b** exhibits endothermic peaks at 64.2°C ($\Delta H = 0.22\,kJmol^{-1}$), 71.4°C ($\Delta H = 17.04\,kJmol^{-1}$), 84.3°C ($\Delta H = 8.29\,kJmol^{-1}$), and 104.6°C ($\Delta H = 0.08\,kJmol^{-1}$), which define the subsequent crystal-to-crystal phase transition (polymorphism), and the highest temperature peak 220°C is due to the crystal-to-isotropic liquid phase transition. The exothermic peaks of this compound are observed at 150.5°C ($\Delta H = 0.11\,kJmol^{-1}$), 109.7°C ($\Delta H = 0.15\,kJmol^{-1}$), and 83.3°C ($\Delta H = 16.04\,kJmol^{-1}$), which define isotropic-to-mesophase and mesophase-to-subsequent crystal phase transitions, respectively. Thus, this compound shows significant polymorphic changes in the heating cycle only. The texture of the mesophase observed under polarizing microscope is characteristic of monotropic radial nematic bubbles (droplets) appearing in cooling cycle with disclination within the droplets showing schlieren texture. The defect inside the radial structure is of hedgehog type. The

radial curvature in liquid crystalline system costs energy. The elastic free energy of the nematic mesophase scales with the curvature per unit length. At a high enough curvature, the elastic free energy density of the nematic phase can exceed free energy for melting the nematic into the isotropic phase. In these regions, the nematic director becomes indeterminant and a defect or disclination is formed. The similar phase transition temperature and textural pattern is observed for compounds **4c** and **4d**, except that the latter shows some more polymorphic changes in the heating cycle. The compound **4f** shows endothermic peaks and enthalpy at 64.6°C ($\Delta H = 0.15\,kJmol^{-1}$), 77.4°C ($\Delta H = 2.67\,kJmol^{-1}$), and 84.0°C ($\Delta H = 5.56\,kJmol^{-1}$), showing subsequent crystal-to-crystal phase transitions (polymorphism), and one at 192.0°C exhibits a transition from crystal to isotropic liquid phase. The exothermic peaks at 150.5°C ($\Delta H = 0.16\,kJmol^{-1}$), 109.4°C ($\Delta H = 0.42\,kJmol^{-1}$), 98.1°C ($\Delta H = 1.47\,kJmol^{-1}$), 81.1°C ($\Delta H = 3.57\,kJmol^{-1}$), and 67.1°C ($\Delta H = 3.84\,kJmol^{-1}$) depict



Scheme 1. Synthetic route for 2,5-bis[4-n-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones.

the subsequent crystal to crystal phase transitions. The investigation of the texture under optical microscope reveals no mesomorphic property for this compound both in heating and cooling cycles. Thus, this compound exhibited a rich polymorphism in both the cycles. The similar phase transitions and non-mesomorphic behaviour is observed for compound **4h**. The compounds **4e** and **4g** exhibit sharp endothermic and exothermic peaks corresponding to a sudden phase transition from crystal to isotropic phases at 91.3°C and 67.6°C and subsequent isotropic to crystal phase transition at 69.0°C ($\Delta H = 24.95\,kJmol^{-1}$) and 62.6°C ($\Delta H = 17.74\,kJmol^{-1}$), respectively. The optical analysis revealed no texture for these compounds, and therefore, the compounds, were found to be non-mesogenic in nature.

The structure–mesophase correlation of these compounds reveals that the homologous members of this series are calamitic in nature. The lower members with m = 7, 8, 9, 10 show monotropic nematic phase, and the higher homologs with m = 11, 12, 14, and 16 do not display mesomorphic behavior. The presence of ester bridging group increases flexibility and mobility of particular part of liquid crystal molecule stabilizing the nematic mesophase [14], but as the alkoxy chain length increases, the non-polar ends dominate over the polarity, and molecules are prevented to slide over each other, thereby increasing the intermolecular forces and resulting in the loss of mesogenic property.

Conclusions

A new series of 2,5-bis[4-n-alkoxybenzoyloxy-(4-benzoyloxy)]-3,6-dichloro-1,4-benzoquinones have been synthesized having terminal alkoxy chains (m = 7∼16). The chemical structures of the products were investigated by IR, NMR, UV-visible, ^{1}H, and ^{13}C NMR spectra. The mesomorphic properties and optical textures of the products were characterized by DSC and POM. The existence of nematic (schlieren texture) was confirmed by POM. It was found that the mesogenic nature of these compounds is dependent on the alkoxy chain length. The lower homologues with (m = 7, 8, 9, 10) exhibit monotropic nematic mesophase, whereas the higher homologues were non-mesogenic in nature.

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