

# Synthesis and Liquid Crystalline Evaluation of New Benzoquinone Esters

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**Abstract:-** The synthesis of benzoquinone esters was described. 2, 3, 5, 6-Tetra hydroxy benzoquinone was protected as semicarbazone to avoid hexa ester formation and esterified. This product was hydrolysed to get 2,3,5,6-tetraacyloxy-1,4-benzoquinone. Their phase transition behaviour was investigated by differential scanning calorimetry and textures were photographed at mesophase region by using polarizing optical microscope.

**Key words:** Benzoquinone esters, Discotic liquid crystals, Mesophase, Phase transition temperatures.

## I. INTRODUCTION

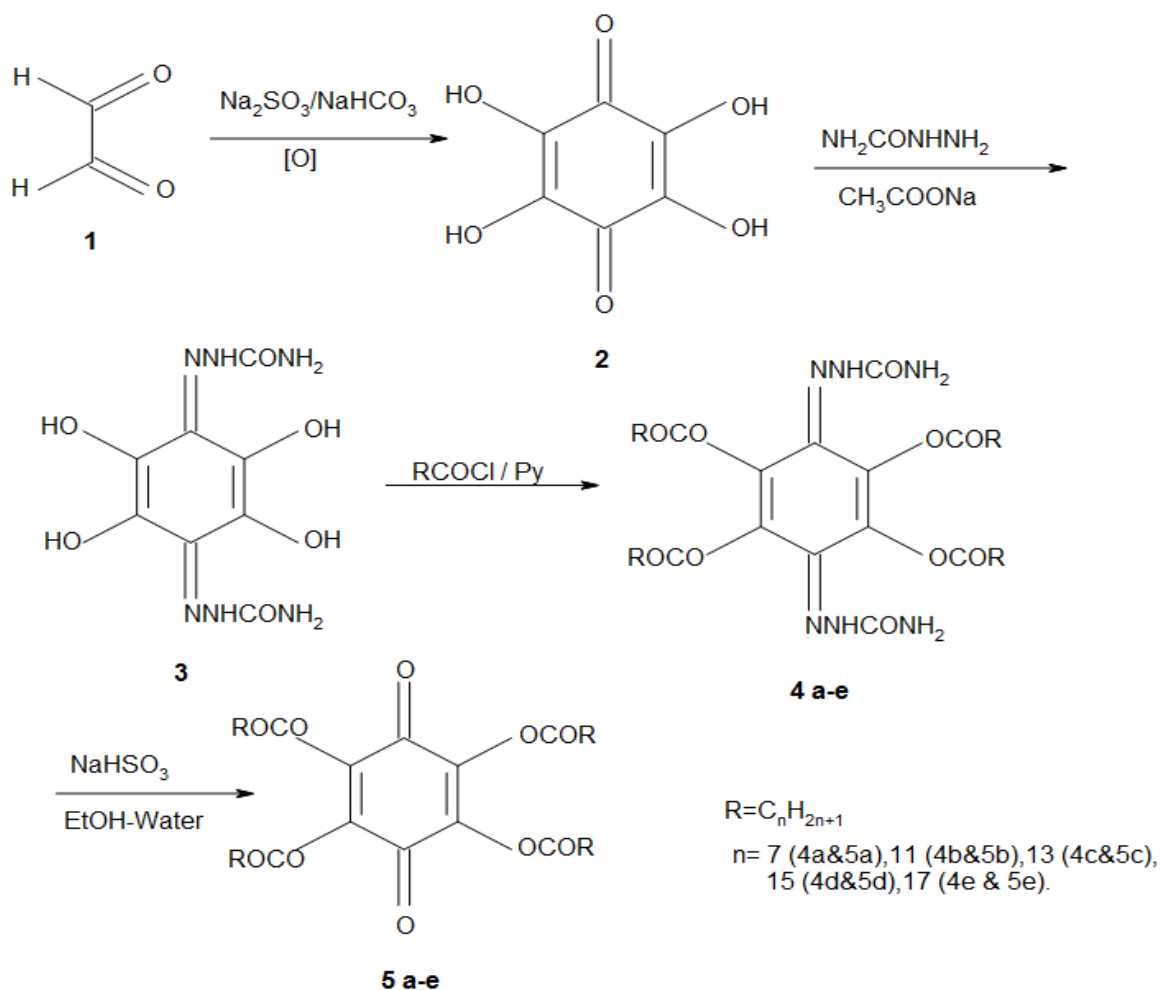
Among the mesogenic polyaromatic cores<sup>1</sup>, hexa substituted derivatives of benzene, triphenylenes<sup>2,3</sup>, truxenes<sup>4-6</sup> and anthraquinones<sup>7,8</sup>, exhibit discotic columnar phases or the least ordered most mobile mesophase, N<sub>D</sub> nematic. Discotic liquid crystals are formed from disc shaped molecules known as “discotic mesogens”. The first report of disc like molecules was proposed by Chandrasekhar et al.<sup>9</sup>, in 1977 and the first investigated compounds are benzene hexa-n-alkanoates. Based on X-ray data the authors proposed a structure, in which the discs are stacked one on top of the other in columns, constitutes a hexagonal arrangement. Benzene hexa heptanoate and octanoate are mesomorphic, but the hexanoate compound shows pressure induced mesomorphism.<sup>10,11</sup> The chemical nature of the aliphatic chain will decides the mesomorphic properties, for instance some hexa substituted benzene derivatives with poly hetero atomic chains are, devoid of mesomorphism.<sup>12</sup>

The columnar liquid crystalline molecules have a pi electron aromatic core, attached by flexible alkyl chains. The aromatic core allows charge transfer, through the  $\pi$  conjugate systems and the alkyl chains act as insulating material. This feature leads to new discoveries in molecular electronics and have potential applications in organic light emitting diodes<sup>13,14</sup>, molecular wires<sup>15</sup> and photovoltaic devices.<sup>16</sup>

In this present investigation, it is proposed to synthesize 2,3,5,6-tetraacyloxy-1,4-benzoquinone's (**5 a-e**) and study their liquid crystal properties. Fatiadia et al.<sup>17</sup>, synthesized 2,3,5,6-tetrahydroxy-1,4-benzo quinone (**THBQ**) **2**, starting with glyoxal **1** in the presence of Na<sub>2</sub>SO<sub>3</sub> and NaHCO<sub>3</sub> with good yields. Spasov et al.<sup>18</sup>, reported that tetra hydroxy quinone was refluxed with the corresponding acid chlorides in the presence of magnesium, to give tetra ester of **THBQ**. Many hindered alcohols were esterified under Spasov conditions.<sup>19</sup> A.F.Fatiadi et al.<sup>20</sup>, reported acylation of tetra hydroxy p-benzoquinone in the presence of pyridine gave benzene hexol (hexahydroxy benzene) hexa acetate and rhodizonic acid in nearly equal proportions, but not the tetra acetate of tetra hydroxy quinone. Our attempts to synthesize the same, were not successful and we isolated hexa esters instead of tetra esters, in that route. Now, we will explain our synthetic approach (**Scheme-1**), by considering the synthesis of compound **5b**.

### *Synthesis of 2,3,5,6-Tetra lauroyloxy-1,4-benzo quinone 5b*

In order to achieve the objective, the ketonic groups of **THBQ** were protected as semicarbazones and refluxed with lauroyl chloride in the presence of pyridine under anhydrous conditions, resulting compound **4b**, which was recrystallized from chloroform– methanol. The infra-red spectrum showed a peak 3459, 3362 (-NH str), 1789 (ester carbonyl) cm<sup>-1</sup>, confirming the formation of **4b**. Further the <sup>1</sup>H nmr spectrum showed 0.82 – 0.93 (t, 12H, 4xCH<sub>3</sub>), 1.2 – 1.38 (br.s, 72 H, 36 x CH<sub>2</sub>), 2.2 – 2.4 (m, 8H, 4x OCOCH<sub>2</sub>), 2.9 and 3.08 (NH protons) confirms the formation of tetra lauroyloxy quinone semicarbazone **4b**. The esterified semicarbazone **4b** was cleaved with sodium bisulfite<sup>21</sup> resulting the formation of 2,3,5,6-tetra lauroyloxy-1,4-benzoquinone **5b**.



The purity of the compound was checked by HPLC, which was 99.67%. The I.R. spectrum showed absorption bands at 2960, 2922 (C-H str.), 1713 (C=O str.). The  $^1\text{H}$  nmr spectrum showed  $\delta$  0.9 (t, 12H, 4 x  $\text{CH}_3$ ), 1.2 – 1.4 (br.s, 72H, 36 x  $\text{CH}_2$ ), 2.25-2.35 (t, 8H, 4 x  $\text{OCOCH}_2$ ). The above data is in good agreement with the reported data by H.S. Verter et al.<sup>22</sup>

Similarly the other tetra acyloxy benzoquinones, were synthesized. The  $^1\text{H}$  nmr data of these compounds was presented in table-1. The DSC thermo grams were recorded and the data was presented in table-2. The textures were photographed at the mesophase region with the aid of polarizing optical microscopy (POM) (Fig. 1, 2 & 3).

Table – 1

$^1\text{H}$  nmr spectral data of 2,3,5,6- tetra acyloxy-1,4- benzoquinones (5 a-e)

Compound	$^1\text{H}$ nmr spectral data
5a	$\delta$ 0.8 (t, 12H, 4 x $\text{CH}_3$ ), 1.1 – 1.33 (br.s, 40H, 20 x $\text{CH}_2$ ), 2.31 – 2.42 (t, 8H, 4 x $\text{OCOCH}_2$ )
5b	$\delta$ 0.9 (t, 12H, 4 x $\text{CH}_3$ ), 1.2 – 1.4 (br.s, 72H, 36 x $\text{CH}_2$ ), 2.25 – 2.35 (t, 8H, 4 x $\text{OCOCH}_2$ )
5c	$\delta$ 0.85 (t, 12H, 4 x $\text{CH}_3$ ), 1.15 – 1.38 (br.s, 88H, 44 x $\text{CH}_2$ ), 2.15 – 2.4 (t, 8H, 4 x $\text{OCOCH}_2$ )
5d	$\delta$ 0.92 (t, 12H, 4 x $\text{CH}_3$ ), 1.2 – 1.32 (br.s, 104H, 52 x $\text{CH}_2$ ), 2.23 – 2.48 (t, 8H, 4 x $\text{OCOCH}_2$ )
5e	$\delta$ 0.8 – 0.85 (t, 12H, 4 x $\text{CH}_3$ ), 1.2 – 1.5 (br.s, 120H, 60 x $\text{CH}_2$ ), 2.23 – 2.45 (t, 8H, 4 x $\text{OCOCH}_2$ )

Table – 2  
Phase transition temperatures (PTT) and heat of transition ( $\Delta H$ ) of compounds 5a-e

Phase	Compound 5a		Compound 5b		Compound 5c		Compound 5d		Compound 5e	
	PTT °C	$\Delta H$ J/g	PTT °C	$\Delta H$ J/g	PTT °C	$\Delta H$ J/g	PTT °C	$\Delta H$ J/g	PTT °C	$\Delta H$ J/g
Crystal – mesophase $K \rightarrow S_1$	-	-	43.0 – 63.84	146.3	34.55 – 56.8	95.69	63.27 – 77.84	146.6	53.57 – 71.79	114.5
Mesophase- mesophase $S_1 \rightarrow S_2$	78.85 – 132.4	17.3	200.94 – 274.36	165.3	246.9 – 287.1	57.14	207.7 – 226.5	3.154	176.6 – 184.4	1.68
Mesophase – mesophase $S_2 \rightarrow S_3$	179.8 – 243.2	51.11	321.76 – 365.82	10.15	389.7 – 419.2	13.18	245.5 – 261.7	21.58	441.9 – 475.2	30.5
Mesophase – mesophase $S_3 \rightarrow S_4$	258.5 – 289.6	43.13	413.87 – 450.3	61.89	430.3 – 512.7	9.388	269.1 – 294.3	34.2	-	-
Mesophase- Isotropic $S_4 \rightarrow I$	340.1 – 508.2	530.2	457.45 – 512.74	81.42	482.3 – 539.1	23.13	481.8 – 548.2	294.8	529.9 – 563.7	334.6



Fig.1. "POM Texture", on cooling the mesophase of compound 5b.



Fig.2. "POM Texture", on cooling the mesophase of compound 5e.

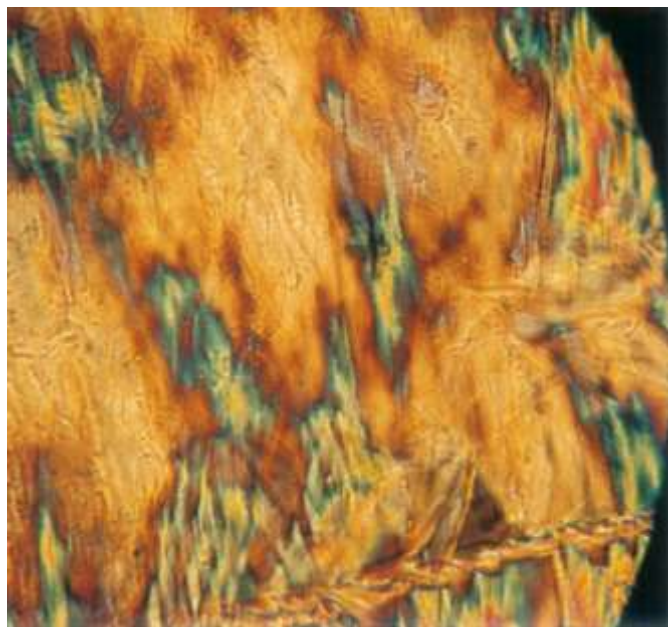


Fig.3. "POM Texture", on cooling the mesophase of compound 5a.

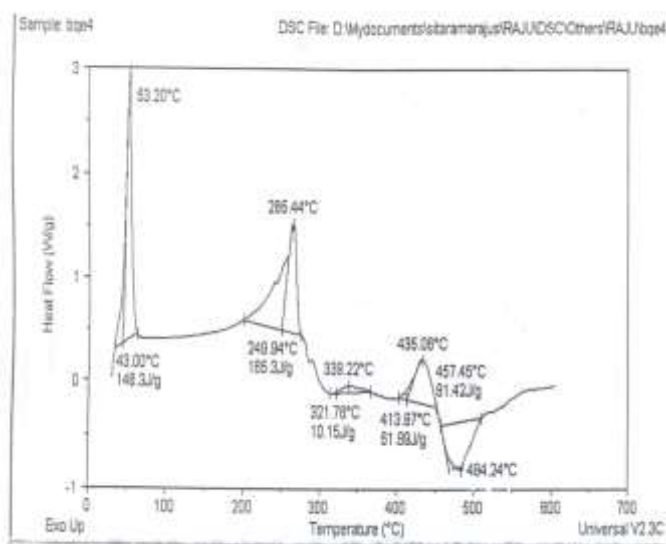


Fig. 4. DSC thermogram of 2,3,5,6-Tetra lauroyloxy-1,4-benzo quinone 5b

## II. EXPERIMENTAL

### General Information

$^1\text{H}$  nmr spectra was recorded on BRUKER AMX-400 spectrometer operating at 400 MHz. IR spectra was recorded on Perkin-Elmer 841 infra red spectrophotometer or NICOLET AVATAR-320-FT-IR spectrophotometer. The purity of the compounds were checked on TLC and HPLC(SHIMADZU-LC 6A). All materials were reagent grade and used as received without further purification.

### Synthesis of 2,3,5,6-tetrahydroxy-1,4-benzo quinone (THBQ) 2

The compound **2** was synthesized from glyoxal according to the procedure of Fatiadi et al.<sup>20</sup> In a 5 litre three-necked round bottomed flask, a solution of 200 g (1.586 mol) of anhydrous sodium sulfite and 75 g (0.89 mol) of anhydrous sodium bicarbonate in 2 litres of water was taken and heated to 40-45°C. 300 g (240 ml, 1.55 mol) of 30% glyoxal solution was added to this and a brisk stream of air or oxygen was passed through the solution for 1 hour without application of heat. Now the reaction flask was heated to 80-90°C over a period of 2 hrs. The air current is then stopped and the mixture is heated to incipient boiling and left over night. The sodium salt of **THBQ** was filtered and washed successively with 50 ml of cold 15% NaCl solution, 50 ml of cold 1 : 1, methanol : water and 50 ml of cold methanol. The air dried salt weighed 12 g.

This salt was taken in a 250 ml conical flask and 150 ml of 2N hydrochloric acid was added and heated to incipient boiling. The resultant solution was cooled in an ice bath, and the glistening black crystals of **THBQ** that precipitated were filtered and washed with ice water to gave 7.4 g of the product.

### Synthesis of Semicarbazone of THBQ 3

Semicarbazide hydrochloride (0.02 mol) and fused sodium acetate (0.03 mol) was dissolved in 10-20 ml of water. **THBQ** (**2**) (0.01 mol) was dissolved in 10-15 ml of acetone free alcohol and was added to the above solution. The reaction mixture was heated for 40 minutes at 50-60°C and left over night. The product was filtered and washed with water, yielded blackish green crystals of semicarbazone of **THBQ**.

M.p. 318°C.; IR  $\nu_{\text{max}}^{\text{Neat}}$  : 3459,3362 (br., amino group and hydroxyl group), 1730 (C = O str.), and 1674 (C=N str.)  $\text{cm}^{-1}$ .  $^1\text{H}$  nmr (DMSO/TMS):  $\delta$  3.45 (br.s., NH), 14.0 (br.s., 4H, phenolic hydroxyl).

### Synthesis of 2,3,5,6-tetra octanoyloxy-1,4-benzo quinone semicarbazone 4a

Compound **3** (0.01 mol) was dissolved in 15 ml of pyridine and octanoyl chloride (0.04 mol) was added and refluxed for 5 hr., under anhydrous conditions. The reaction mixture was worked up and washed with 5%  $\text{NaHCO}_3$ , 5% HCl and water, repeatedly, dried over anhydrous  $\text{MgSO}_4$  and evaporation of the solvent yielded compound **4a**, which is recrystallized from chloroform – methanol. IR  $\nu_{\text{max}}^{\text{CHCl}_3}$  : 3750 (N-H str.) and 1789 (C=O str.)  $\text{cm}^{-1}$ .  $^1\text{H}$  nmr ( $\text{CDCl}_3/\text{TMS}$ ):

$\delta$  0.7 - 0.9 (t, methyls), 1.2 - 1.8 (br.s, methylenes), 2.1 (t, 8H, -OCOCH<sub>2</sub>), 3.1- 3.2 (br.s, NH).

According to the general process mentioned above, compounds **4b-e** were synthesized and characterized by their nmr and IR spectral data.

#### Synthesis of 2,3,5,6-tetra octanoyloxy-1,4-benzo quinone **5a**

Compound **4a** (0.01mol) was dissolved in 100 ml of 50% aqueous ethanol and was refluxed with 0.02 mol of NaHSO<sub>3</sub>. After completion of the reaction, this was extracted with CHCl<sub>3</sub> and washed with dilute HCl, water and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent results, pale yellow needles. IR  $\nu_{\max}^{\text{CHCl}_3}$ : 1781 (ester carbonyl), 1642 ( $\alpha,\beta$  - unsaturated ketone). <sup>1</sup>H nmr (CDCl<sub>3</sub>/TMS):  $\delta$  0.8 (t, 12H, 4x CH<sub>3</sub>), 1.1 – 1.33 (br.s, 40H, 20 x CH<sub>2</sub>) and 2.31-2.42 (t, 8H, -OCOCH<sub>2</sub>).

Similarly compounds **5 b-e**, were synthesized and characterized by physical and spectral methods.

### III. RESULTS AND DISCUSSION

#### Mesomorphic properties

This report supports the mesomorphic behaviour of benzoquinone esters. All the esters form stable mesophases over narrow temperature range. The phases exhibits fine mosaic texture and high viscosity. Based upon these facts we are proposing that, the mesophases were columnar. Observation of the mesophases and the data from table-2, it is interesting to note that all the esters exhibited minimum four liquid crystal phases and in particular, compounds **5b**, **5c** and **5d** exhibiting five mesophases. This is in accordance with our targeted aim of synthesizing liquid crystals having, more than four mesophase regions. All the esters showed mesophase range of 10 – 16°C during the first liquid crystal phase (K – S<sub>1</sub>), and also for other mesophases the data is as expected. In case of compounds **5a**, it is observed that a high heat of transition of 530.2 J/g during the mesophase S<sub>4</sub>-Isotropic I (S<sub>4</sub> – I).

### IV. CONCLUSIONS

A series of **THBQ** esters were prepared. All the ester molecules exhibited liquid crystalline properties. The accuracy of phase transition temperatures was satisfactory.

The observed temperatures for the solid-liquid crystal and liquid crystal-liquid transitions were meticulous.

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