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## Liquid Crystals

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## Preliminary communication

# Liquid crystalline properties in a series of disc-like compounds with two long alkyloxy chains attached to the core

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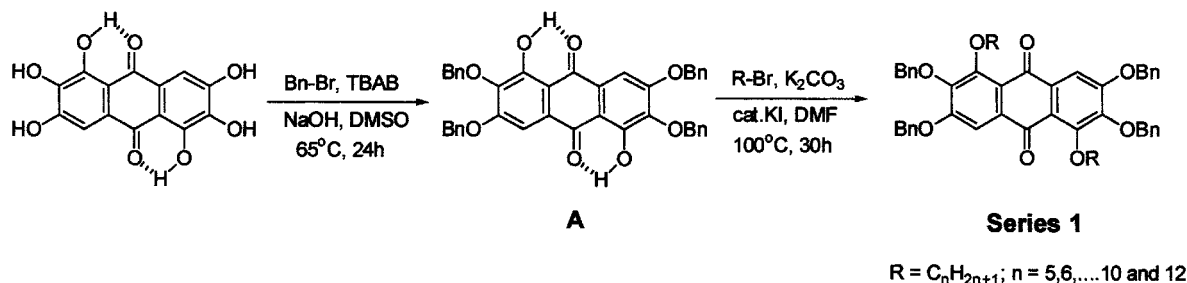
We report the synthesis and characterization of a novel series of anthraquinone-based discotic liquid crystals, viz. 1,5-dialkyloxy-2,3,6,7-tetrakis(benzyloxy)anthra-9,10-quinones. To our knowledge, these are the first examples of discotic liquid crystals wherein only two, long flexible aliphatic chains are attached to the core. The rest of the four positions are substituted with bulky benzyloxy groups. Most of the compounds synthesized in this series are found to be liquid crystalline. They exhibit the typical texture of a columnar mesophase. Further, these compounds can serve as useful precursors for obtaining various unsymmetrical derivatives of 9,10-anthraquinones.

Since the discovery of discotic liquid crystals [1], a large number of disc-like organic molecules have been found to form columnar mesophases. Among these, 9,10-anthraquinone (rufigallol) derivatives are one of the earliest systems reported to form such types of mesophase [2–4]. When we look into the literature of discotic compounds, surprisingly we find that very little work has been carried out on this core. The rufigallol core has six phenolic groups with unequal reactivity. This allows the selective substitution of four phenolic groups leaving unaffected the two intramolecularly hydrogen-bonded hydroxyl groups, and thus various ‘mixed tail’ discotics can be easily prepared [5]. The quinonoid system may behave as an electron acceptor and therefore the systems can be doped with electron donors to prepare n-type conductors [6]. Tetra-, hexa-, and octa-substituted anthraquinone derivatives are known to form discotic liquid crystals. Formation of highly ordered phases on cooling the normal columnar phase is also reported for many of these derivatives [7, 8]. Similar highly ordered phases exhibited by some of the triphenylene derivatives have recently been characterized as discotic plastic and helical phases. Interestingly, the charge carrier mobility in these phases has been found to be one to three orders of magnitude higher than in the normal columnar phase [9, 10].

In both the symmetrically and unsymmetrically substituted derivatives of anthraquinone reported so far, the flexible part consists of normal aliphatic chains

bound to the central core by ether or ester linkages. To understand the structure–property relationships for 9,10-anthraquinone derivatives, we have recently carried out substitution with slightly bulkier pendant groups, viz. benzyloxy groups, on this core at the 1 and 5 positions [11]. Here, some of the derivatives were found to form highly ordered three-dimensional phases in addition to the normal columnar mesophases. When the 1 and 5 positions were substituted with 2-tetrahydropyranyloxyethoxy groups (THP-ethers), formation of only the hexagonal columnar mesophase was observed. The deprotected derivatives of these THP-ethers were found to form a highly ordered ‘discotic plastic’ type of mesophase [12]. Very recently, there has been a report [13] from our laboratory on a monofunctionalized anthraquinone-based discotic liquid crystal which is anticipated to be a potential synthon for making several discotic materials.

As a continuation of our study on structure–property relationships for anthraquinone-based discotic liquid crystals, we have synthesized a series of anthraquinone derivatives, viz. 1,5-dialkyloxy-2,3,6,7-tetrakis(benzyloxy)anthra-9,10-quinones (series 1), as shown in the scheme, where Bn = benzyl. One should notice that, unlike our previous study [11], here we have substituted the bulky benzyloxy groups at the 2,3,6 and 7-positions instead of at the 1 and 5-positions. The 1 and 5-positions are then utilized to attach alkyloxy chains to the anthraquinone core.



Scheme.

Rufigallol was obtained as described in the literature [14]. The crude rufigallol was used for the next step of benzylation. A typical procedure followed to obtain one of the final compounds ( $n = 10$ ) of series 1 is now given.

*1,5-Dihydroxy-2,3,6,7-tetrakis(benzyloxy)anthra-9,10-quinone (A)*: Rufigallol (2.96 g, 0.01 mol), TBAB (14.18 g, 0.044 mol) and NaOH (1.6 g, 0.04 mol in 5 ml of water) were mixed with DMSO (150 ml). The mixture was stirred for 15 min under a nitrogen atmosphere. Benzyl bromide (7.52 g, 0.44 mol) was added to the stirred mixture and reaction was allowed to proceed at 65°C for 24 h under a nitrogen atmosphere. After cooling, the brick-red coloured needle-like crystals of the product were filtered off and the crude product was purified by column chromatography and recrystallization (ethanol/ $CHCl_3$ ). Yield 16%, m.p. 119°C–224.0°C.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$ : 12.81 (s, 2H, Ar-OH), 7.27–7.47 (m, 22H, Ar-H), 5.26 (s, 4H,  $-OCH_2-$ ), 5.24 (s, 4H,  $-OCH_2-$ ).

*1,5-Didecyloxy-2,3,6,7-tetrakis(benzyloxy)anthra-9,10-quinone*: Compound A (0.20 g, 0.3 mmol), 1-bromodecane (0.531 g, 2.4 mmol),  $K_2CO_3$  (0.25 g, 1.8 mmol) and a catalytic amount of KI were mixed in DMF (20 ml). The mixture was heated to 100°C for a period of 30 h under a nitrogen atmosphere. After cooling, the reaction mixture was poured into cold water (50 ml) and the product was extracted into chloroform (30 ml  $\times$  2). The organic layer was washed with distilled water (50 ml  $\times$  3) and dried ( $Na_2SO_4$ ). The crude product obtained after removing the solvent was purified by passing it through basic aluminium oxide using  $CH_2Cl_2$  as eluent. Finally, it was recrystallized twice using ethanol. Yield 41%, m.p. 143.0°C.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$ : 7.74 (s, 2H, Ar-H), 7.29–7.43 (m, 20H, ArH), 5.24 (s, 4H,  $-OCH_2-$ -benzyl), 5.12 (s, 4H,  $-OCH_2-$ -benzyl), 4.09 (t,  $J = 7.0$  Hz, 4H,  $-OCH_2-$ ), 1.28–1.92 (m, 32H,  $-CH_2-$ ), 0.88 (m, 6H,  $-CH_3-$ ). Mass (FAB):  $m/z$  946  $[M + 2]^+$  [calcd. for  $C_{62}H_{72}O_8$ ].

The transition temperatures and the associated enthalpies for the compounds of series 1 are given in the table. As can be seen, except for the first and last homologues, where  $n = 5$  and 12, all are found to be

Table. Transition temperatures ( $^{\circ}C$ ) and enthalpies of transitions ( $kJ\ mol^{-1}$ ) in italics, for the compounds of series 1. Parentheses indicate monotropic transitions.

| $n$ | $Cr_2$                  | $Cr_1$                  | Col                       | I |
|-----|-------------------------|-------------------------|---------------------------|---|
| 5   | • 138.0<br><i>18.91</i> | • 167.5<br><i>36.58</i> | —                         | • |
| 6   | • 147.5<br><i>16.60</i> | • 158.5<br><i>43.0</i>  | • (140.0) <sup>a</sup>    | • |
| 7   | • 124.5<br><i>18.92</i> | • 156.5<br><i>42.57</i> | • (141.0) <sup>a</sup>    | • |
| 8   | • 126.5<br><i>25.14</i> | • 143.5<br><i>36.58</i> | • (134.5)<br><i>12.05</i> | • |
| 9   | • 108.5<br><i>20.41</i> | • 132.5<br><i>31.56</i> | • (128.0)<br><i>12.60</i> | • |
| 10  | —                       | • 118.5<br><i>56.64</i> | • (115.5)<br><i>11.4</i>  | • |
| 12  | —                       | • 120.0<br><i>58.8</i>  | —                         | • |

<sup>a</sup> Enthalpies could not be calculated due to the onset of crystallization.

liquid crystalline. However, the mesophase remained monotropic throughout the series. On cooling from the isotropic liquid they exhibit a ‘flower-like’ texture, typical

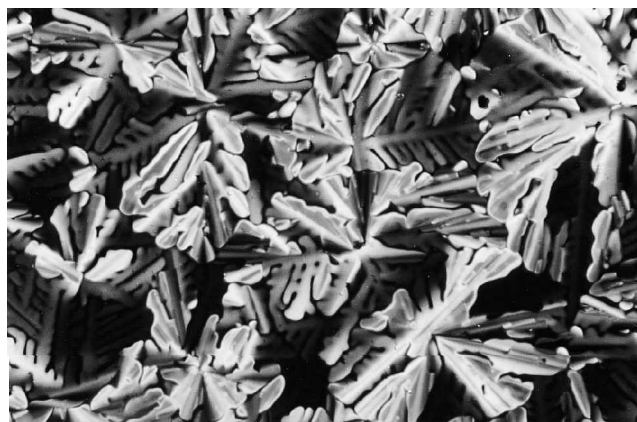


Figure 1. Optical photomicrograph showing the typical ‘flower-like’ texture of a columnar mesophase for the compound with  $n = 10$  at 110°C.

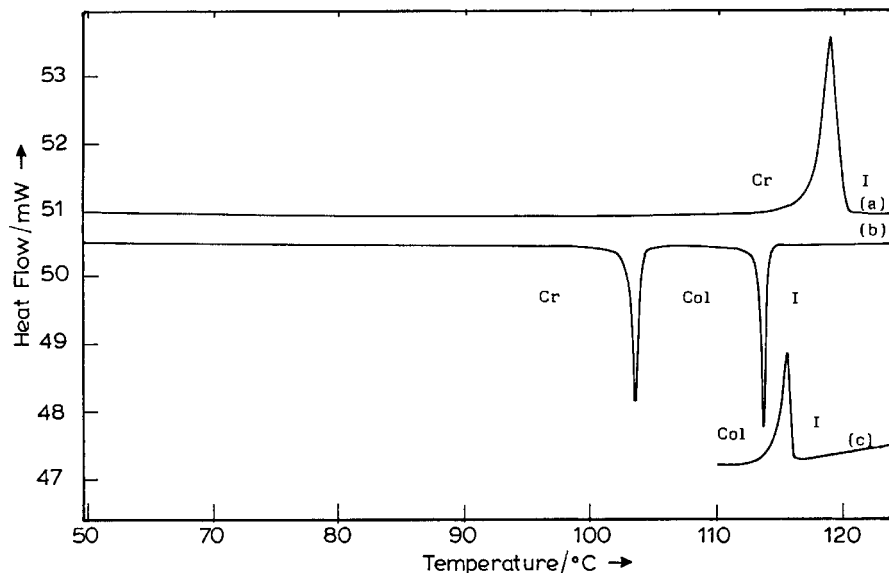


Figure 2. DSC thermograms for the compound with  $n = 10$ . The heating and cooling rate was  $5^{\circ}\text{C min}^{-1}$ . Scan (a) represents the first heating, showing only one peak corresponding to the Cr-I transition; (b) represents the cooling cycle, showing two peaks corresponding to the I-Col and Col-Cr transitions, respectively. Scan (c) confirms the existence of the monotropic columnar mesophase.

of a columnar mesophase. A photomicrograph of this texture taken for the compound with  $n = 10$  is shown in figure 1. The texture is very similar to the one observed for the THP-ethers of 9,10-anthraquinones [12]. This indicates that the mesophase exhibited by the present series of compounds may be hexagonal in nature.

The thermogram obtained by differential scanning calorimetry (DSC-7 Perkin Elmer) for the compound with  $n = 10$ , is shown in figure 2. On first heating (a) we get only one peak which corresponds to the Cr-I transition seen using the microscope. On the cooling cycle (b) from the isotropic liquid to room temperature, we obtain two peaks: the first corresponds to the I-Col transition and the second to the Col-Cr transition, as observed by polarizing optical microscopy. To make sure of the existence of the monotropic columnar mesophase, we cooled the sample until the I-Col peak was obtained, and then reheated the sample immediately. As expected (c), we found the Col-I peak at  $115.5^{\circ}\text{C}$ , which is somewhat lower than the Cr-I transition temperature ( $119.0^{\circ}\text{C}$ ).

Comparing the present series of compounds with the already reported 1,5-dibenzyloxy [11] and 1,5-bis-(2-tetrahydropyranoxyethoxy) [12] derivatives, we find that the latter two series exhibit enantiotropic columnar mesophases with much wider mesophase ranges. However, with the object of preparing a variety of unsymmetrically substituted derivatives of 9,10-anthraquinone, we prepared the present compounds of series 1; indeed, to our surprise, we found these intermediates themselves are mesomorphic. Hence, we studied them in detail. Though,

all six positions of rufigallol are substituted in these compounds of series 1, one should note that, the long flexible alkyloxy chains are substituted at only two positions and the remaining four positions are substituted with much bulkier benzyloxy groups.

To summarize, we report a homologous series of 9,10-anthraquinone-based discotic liquid crystals, viz. 1,5-dialkyloxy-2,3,6,7-tetrakis(benzyloxy)anthra-9,10-quinones. These are the first examples of discotic mesogens wherein only two, long flexible aliphatic chains are attached to the core. Most of the compounds synthesized in this series are found to be liquid crystalline, forming a monotropic columnar mesophase. These compounds can serve as useful precursors for further derivatization of this core. Deprotection of these benzyl ethers (series 1) by hydrogenolysis and substitution with different groups at the 2,3,6,7-positions of the resultant deprotected products are presently in progress.

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