# Room-temperature electron-deficient discotic liquid crystals: facile synthesis and mesophase characterization

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Two novel series of rufigallol-based room-temperature discotic liquid crystals have been designed and synthesized using microwave dielectric heating within a few minutes in good yield. The chemical structures of all the compounds have been characterized using spectral techniques and elemental analysis. The mesophase behaviors of all the compounds have been investigated by polarizing optical microscopy and differential scanning calorimetry. Columnar hexagonal structure of the mesophase of these compounds has been established with the help of X-ray diffraction studies.



## Introduction

Liquid crystals are unique functional self-organized soft-materials which possess order and dynamics. Recently liquid crystals formed by disc-shaped molecules have been attracting growing interest.[1] Discotic liquid crystals (DLCs) are unique nanostructures with remarkable electronic and optoelectronic properties. The supramolecular assembly of discotic liquid crystals are of fundamental importance not only as models for the study of the energy and charge migration in self-organized systems but also as functional materials for device applications such as one-dimensional conductors, photoconductors, light-emitting diodes, photovoltaic solar cells and gas sensors. The functional capabilities of these materials are due to their easier processibility, spontaneous alignment between electrodes and self-healing of defects owing to their dynamic nature. To realize these potential applications, discotic liquid crystals having mesophase at room temperature and mesophase stability over a wide temperature range with a single mesophase structure is desired.

In the design of discotic liquid crystals the use of branched alkyl chains to modify thermal properties is well documented.[2] It is realized that the use of branched alkyl chains generally does not change the nature of the mesophase, but reduces the transition temperatures, broadens the mesophase range and helps in obtaining room-temperature liquid crystalline materials. This strategy has been applied to phthalocyanines,[3] hexabenzocoronenes,[4] tricycloquinazolines,[5] and alkynylbenzenes[6] to obtain room-temperature liquid crystalline phases, which could be due to steric crowding and stereoheterogeneity introduced by the branched chains.

Rufigallol has been found to function as the core fragment for a remarkable family of discotic liquid crystals.[7] Rufigallol derivatives are one of the earliest systems reported to form columnar mesophases. They are interesting materials as these molecules have an elongated core with a two-fold symmetry axis, they are coloured and exhibit important polymorphism, the core is electron-deficient in nature, they are thermally stable, their chemistry is fairly easy and the unequal reactivity of the hydroxyl groups of rufigallol provides the opportunity to prepare unsymmetrical derivatives. Billard and co-workers[7] reported the first discotic liquid crystalline hexaesters of rufigallol in 1980 and since then about 100 different discotic liquid crystalline derivatives of this molecule have been prepared and studied[8] which is rather less as compared to its predecessor triphenylene of which more than 500 discotic liquid crystalline derivatives are known.[9]

Microwave-assisted high-speed chemical synthesis has attracted a considerable amount of attention in the past decade. Almost all types of organic reactions have been performed using the efficiency of microwave-flash heating. This is not only due to the fact that reactions proceed significantly faster and more selectively than under conventional thermal conditions but also because of the operational simplicity, high yield of products and cleaner reactions with easier work-up. A large number of review articles provide extensive coverage of the subject.[10]

Recently we are interested in the synthesis of liquid crystalline materials by the use of microwave dielectric heating[11,12] and use branched alkyl chains to obtain room-temperature liquid crystalline compounds.[5,6,12] Here we present two novel series of rufigallol-based room-temperature electron-deficient discotic liquid crystals obtained by the use of branched alkyl chains with the help of microwave dielectric heating.

## Experimental

### General information

Microwave irradiation was performed in an unmodified household microwave oven (LG, MS-192W). However, commercial microwave reactors for organic reactions are now available which provides adequate mixing and control of reaction parameters such as temperature and pressure. Column chromatographic separation was performed on silica gel (100–200 mesh). $^{1}$H NMR spectra and $^{13}$C NMR spectra

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were recorded in $CDCl_3$ on a 400 MHz (Bruker AMX 400) spectrometer. All chemical shifts are reported in $\delta$ (ppm) units downfield from tetramethylsilane (TMS) and $J$ values are reported in Hz. FT-IR spectra were recorded as KBr discs on Shimadzu FTIR-8400. Elemental analysis was performed on Carlo-Erba Flash 1112 analyser. Transition temperatures were observed using a Mettler FP82HT hot stage and FP90 central processor in conjunction with an OLYMPUS BX51 polarizing microscope. Transition temperatures and associated enthalpies were measured by differential scanning calorimetry heating from −30 °C to isotropic temperatures at the scan rate of 5 °C $min^{-1}$ (Perkin-Elmer Model Pyris 1D with Intracooler 2P cooling system). X-Ray diffraction measurements were carried out using Cu-K$\alpha$ radiation ($\lambda$ = 1.54 Å) generated from a 4 kW rotating anode generator (Rigaku Ultrax-18) equipped with a graphite crystal monochromator. Samples were filled in Hampton research capillaries (0.5 mm diameter) from the isotropic phase, sealed and held on a heater. For all the samples, X-ray diffraction was carried out at room-temperature (25 °C) and diffraction patterns of the mesophase were recorded on a two-dimensional image plate (Marresearch).

Rufigallol **2**, tetraalkoxyrufigallol **3a–i** and **5**, hexaalkoxyrufigallol **4a–i** were prepared as reported.[12]

### Preparation of 6a–i

In a vial containing **5** (0.1 mmol), cesium carbonate (0.6 mmol), and *n*-alkyl bromide (0.6 mmol) was added NMP (0.5 mL). The vial was loosely sealed with a rubber septum and then irradiated in a microwave oven for 30 s. The vial was removed from the oven and left to stand for about 1 min and again irradiated for 30 s. This process was repeated 6–8 times until the reaction was complete (TLC monitoring). The reaction mixture was poured into cold water and the product extracted with dichloromethane. The organic extract was dried, concentrated and the product purified by column chromatography over neutral alumina. Finally the product was crystallized from chloroform by adding excess of ethanol to afford 80–90% of **6a–i**.

### Spectral data

**4e**: $^1$H NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$ 7.6 (s, 2H, Ar-H), 4.1 (m, 12H, ArOC$H_2$), 1.1–2.1 (m, 68H, aliphatic CH and $CH_2$), 0.96 (d, 6H, $J$ = 6.2 Hz, $CH_3$), 0.92 (t, 12H, $J$ = 6.7 Hz, $CH_3$), 0.86 (d, 12H, $J$ = 6.6 Hz, $CH_3$). Derivatives **4a–4i** showed similar spectra except for different numbers of aliphatic protons; **4e**, $^{13}$C NMR (100 MHz; $CDCl_3$; $Me_4Si$) $\delta_C$ 181.1, 157.4, 153.9, 146.9, 132.6, 120.3, 106.9, 74.0, 73.1, 69.1, 39.3, 37.4, 31.7, 30.3, 29.8, 29.4, 29.2, 29.0, 27.9, 26.0, 24.6, 22.6, 19.6, 14.0. Derivatives **4a–4i** showed similar spectra; **4e**, FT-IR $\nu_{max}$(KBr)/$cm^{-1}$ 2924, 2852, 1666, 1572, 1464, 1377, 1319, 1265, 1130, 1096, 1040, 978, 876, 721; All other derivatives give similar spectra.

**5**: $^1$H NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$ 12.76 (s, 2H, Ar-OH), 7.4 (s, 2H, Ar-H), 4.23–4.13 (m, 8H, ArOC$H_2$), 1.9–1.1 (m, 40H, aliphatic $CH_2$ and CH), 0.98 (d, 6H, $J$ = 6.3 Hz, –CHC$H_3$), 0.95 (d, 6H, $J$ = 6.6 Hz, –CHC$H_3$), 0.88 (d, 12H, $J$ = 4.5 Hz, –CH(C$H_3$)$_2$), 0.85 (d, 12H, $J$ = 4.5 Hz, –CH(C$H_3$)$_2$); $^{13}$C NMR (100 MHz; $CDCl_3$; $Me_4Si$) $\delta_C$ 186.4, 158.1, 157.3, 141.2, 128.9, 111.8, 104.8, 72.1, 67.8, 39.3, 37.3, 36.1, 31.1, 29.8, 29.7, 28.8, 28.0, 24.7, 22.6, 19.6; FT-IR $\nu_{max}$(KBr)/$cm^{-1}$ 2922, 2854, 1616, 1569, 1506, 1456, 1427, 1365, 1315, 1280, 1226, 1138, 1095, 1045, 950, 864, 802, 723.

**6d**: $^1$H NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$ 7.6 (s, 2H, Ar-H), 4.0–4.2 (m, 12H, ArOC$H_2$), 1.1–1.9 (m, 64H, aliphatic CH and $CH_2$), 0.98 (d, 6H, $J$ = 6.2 Hz, $CH_3$), 0.94 (d, 6H, $J$ = 6.5 Hz, $CH_3$), 0.86 (m, 30H, $CH_3$). Derivatives **6a–6i** showed similar spectra except for different numbers of aliphatic protons; **6d**, $^{13}$C NMR (100 MHz; $CDCl_3$; $Me_4Si$) $\delta_C$ 181.2, 157.5, 153.9, 147.0, 132.7, 120.4, 117.7, 107.0, 74.7, 72.4, 67.5, 39.2, 37.3, 36.1, 31.8, 30.3, 29.7, 29.5, 29.3, 27.9, 26.0, 24.7, 22.6, 19.6, 14.0. Derivatives **6a–6i** showed similar spectra; **6d**, FT-IR $\nu_{max}$(KBr)/$cm^{-1}$ 2924, 2852, 1666, 1572, 1508, 1466, 1377, 1319, 1267, 1130, 1094, 1045, 954, 874, 721. Derivatives **6a–6i** showed similar spectra.

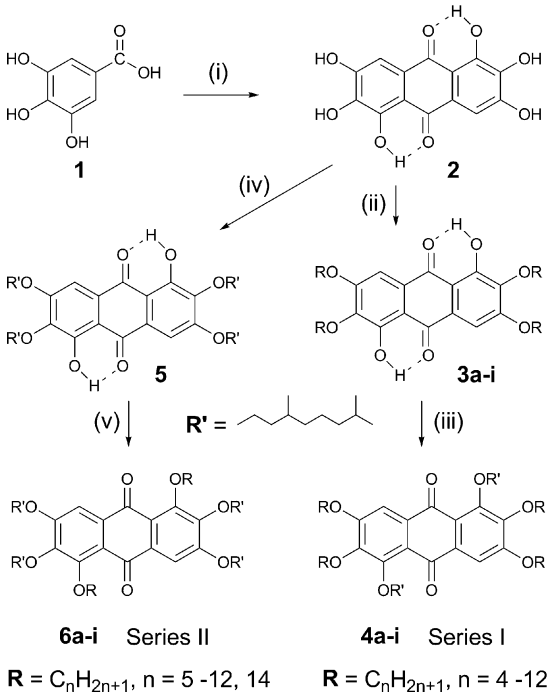
### Elemental analysis data

**4a**, Found: C, 74.69; H, 9.60. $C_{50}H_{80}O_8$ requires 74.22; H, 9.97%. **4b**, Found: C, 75.44; H, 10.54. $C_{54}H_{88}O_8$ requires C, 74.96; H, 10.25%. **4c**, Found: 75.87; H, 10.26. $C_{58}H_{96}O_8$ requires C, 75.61; H, 10.50%. **4d**, Found: C, 75.92; H, 11.0. $C_{62}H_{104}O_8$ requires C, 76.18; H, 10.72%. **4e**, Found: C, 76.47; H, 11.25. $C_{66}H_{112}O_8$ requires C, 76.69; H, 10.92%. **4f**, Found: C, 77.29; H, 11.09. $C_{70}H_{120}O_8$ requires C, 77.15; H, 11.10%. **4g**, Found: C, 77.48; H, 10.95. $C_{74}H_{128}O_8$ requires C, 77.57; H, 11.26%. **4h**, Found: C, 77.65; H, 11.25. $C_{78}H_{136}O_8$ requires C, 77.95; H, 11.41%. **4i**, Found: C, 78.05; H, 11.36. $C_{82}H_{144}O_8$ requires C, 78.29; H, 11.54%. **5**, Found: C, 75.0; H, 10.71. $C_{54}H_{88}O_8$ requires C, 74.96; H, 10.25%. **6a**, Found: C, 76.74; H, 11.26. $C_{64}H_{108}O_8$ requires C, 76.45; H 10.83%. **6b**, Found: C, 76.81; H, 11.64. $C_{66}H_{112}O_8$ requires C, 76.69; H, 10.92%. **6c**, Found: C, 76.84; H, 11.27. $C_{68}H_{116}O_8$ requires C, 76.93; H, 11.01%. **6d**, Found: C, 77.30; H, 10.86. $C_{70}H_{120}O_8$ requires C, 77.15; H, 11.1%. **6e**, Found: C, 77.30; H, 11.53. $C_{72}H_{124}O_8$ requires C, 77.37; H, 11.18%. **6f**, Found: C, 77.85; H, 11.80, $C_{74}H_{128}O_8$ requires C, 77.57; H, 11.26%. **6g**, Found: C, 77.60; H, 11.81. $C_{76}H_{132}O_8$ requires C, 77.76; H, 11.33%. **6h**, Found: C, 77.84; H, 11.82. $C_{78}H_{136}O_8$ requires C, 77.95; H, 11.41%: **6i**, Found: C, 77.92; H, 11.35. $C_{82}H_{144}O_8$ requires C, 78.29; H, 11.54%.

## Results and discussion

### Synthesis

The synthesis of the unsymmetrical hexaethers was achieved by a two-step alkylation process. The unequal reactivity of the six phenolic groups, two of which are less reactive by virtue of being intramolecularly hydrogen bonded to the adjacent quinone carbonyls, was exploited. Etherification of rufigallol **2** under mild conditions produced 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone (**3a–i** and **5**) without alkylating the hydrogen bonded C-1 and C-5 positions. These tetraalkoxy derivatives were further alkylated with the help of microwave dielectric heating as shown in Scheme 1 under mild basic conditions to give the unsymmetrical hexaethers in very good




**Scheme 1** Synthesis of novel liquid crystalline rufigallol derivatives. *Reagents and conditions*: (i), (ii), (iii) as given in ref. 12; (iv) R′Br, DMSO, NaOH, 90 °C 20 h, 35%; (v) RBr, $Cs_2CO_3$, NMP, MW, 3–4 min 80–90%.

yield within 3–4 min which is simple, efficient, rapid and economic. It should be noted that under classical reaction conditions no product could be obtained in such a short reaction time. The optimized yield under microwave dielectric heating condition is 90% in 4 min whereas under classical thermal heating conditions the yield is 65% after 20 h of reaction at 100 °C with identical reaction mixtures.

### Mesophase behavior

The phase transition temperatures of all the compounds were initially established from the polarizing optical microscopy (POM) and then measured accurately by differential scanning calorimetry (DSC) along with their associated enthalpy changes which are listed in Table 1. These materials under crossed polarizers display characteristic defect textures for the columnar hexagonal mesophase upon cooling from isotropic melt, examples of which are shown in Fig. 1(a)–(c). The solvent crystallized samples which exhibit liquid crystalline behavior at room-temperature do not exhibit any characteristic texture at room temperature itself but when cooled from the isotropic liquid they show characteristic broken fan and mosaic textures of discotic columnar phases. However, these compounds possess sufficient mobility at room temperature so that they can be easily sheared. As compared to the compounds of *Series I* the compounds of *Series II* possess more fluidity at room temperature as has been observed under polarizing optical microscope. Surprisingly the branched chain substituted tetraalkoxy-dihydroxy compound **5** exhibits liquid crystalline behavior at room temperature contrary to its straight chain analogous **3a–i** which do not show any liquid crystalline property except compound **3a** which exhibits a metastable monotropic mesophase,[7] this could be because the branched chains fill the necessary space around the core to induce mesomorphism in compound **5**. Compound **5** also forms large homeotropic domains when cooled from the isotropic state as shown in Fig. 1(b). As a typical example the DSC thermogram of compound **5** is shown in Fig. 2. This compound shows only one transition Col–I at 115.7 °C while heating and I–Col transition at 114 °C while cooling, which is the widest mesophase range amongst all the rufigallol derivatives known to date.[8] In *Series I*, the compound **4a** shows a crystalline phase at room temperature and on heating it melts to a columnar liquid crystalline phase at 54.7 °C which clears to an isotropic liquid at 65.8 °C, upon cooling it shows two transitions, I–Col transition at 63.9 °C and another transition at 12.4 °C. The second transition is suspected to be a transition to another mesophase because of the transition enthalpy value *i.e.* 5 kJ $mol^{-1}$ which is of similar magnitude as that of columnar phase transitions. Compounds **4a–4f** display

**Table 1** Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ $mol^{-1}$, in parentheses) of novel rufigallol based discotics; Cr = crystal, $Col_h$ = hexagonal columnar phase, M = unidentified phase, I = isotropic phase

| Compound (*n*) | Heating | Cooling |
|---|---|---|
| **4a** (4) | Cr 54.7 (18.4) $Col_h$ 65.8 (7.6) I | I 63.9 (7.7) $Col_h$ 12.4 (5.0) M |
| **4b** (5) | $Col_h$ 75.2 (9.3) I | I 73.2 (9.1) $Col_h$ |
| **4c** (6) | $Col_h$ 77.7 (9.8) I | I 76.0 (9.9) $Col_h$ |
| **4d** (7) | $Col_h$ 78.7 (9.7) I | I 76.4 (9.6) $Col_h$ |
| **4e** (8) | $Col_h$ 72.3 (9.2) I | I 70.4 (9.2) $Col_h$ |
| **4f** (9) | $Col_h$ 67.4 (8.0) I | I 65.4 (8.0) $Col_h$ |
| **4g** (10) | Cr 37.6 (14.3) $Col_h$ 61.0 (8.0) I | I 59.0 (7.9) $Col_h$ |
| **4h** (11) | Cr 42.0 (56.5) $Col_h$ 54.7 (5.7) I | I 51.7 (5.7) $Col_h$ −28 (9.8) M |
| **4i** (12) | Cr 39.8 (47.8) I | I 30.5 (2.0) $Col_h$ 9.0 (56.6) Cr |
| **5** | $Col_h$ 115.7 (5.5) I | I 114.1 (5.4) $Col_h$ |
| **6a** (5) | Cr 52.6 (34.9) I | I 33.1 (5.8) $Col_h$ |
| **6b** (6) | Cr 57.2 (34.5) I | I 41.3 (6.3) $Col_h$ |
| **6c** (7) | $Col_h$ 52.6 (8.3) I | I 50.7 (8.3) $Col_h$ |
| **6d** (8) | $Col_h$ 56.8 (8.9) I | I 54.6 (8.9) $Col_h$ |
| **6e** (9) | $Col_h$ 59.7 (9.9) I | I 57.8 (9.9) $Col_h$ |
| **6f** (10) | $Col_h$ 59.6 (10.1) I | I 57.6 (10.0) $Col_h$ |
| **6g** (11) | $Col_h$ 56.1 (9.4) I | I 53.9 (9.2) $Col_h$ |
| **6h** (12) | $Col_h$ 52.7 (9.1) I | I 50.4 (8.5) $Col_h$ |
| **6i** (14) | $Col_h$ 39.2 (6.4) I | I 36.1 (6.7) $Col_h$ |

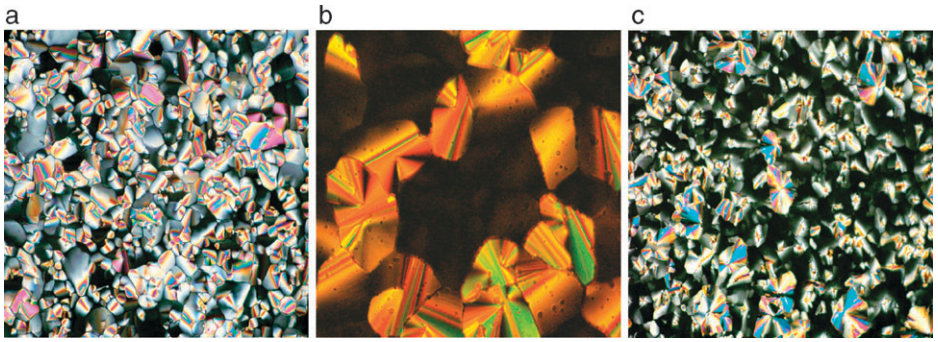



**Fig. 1** Optical photomicrographs of **4e** (a), **5** (b) and **6d** (c) at 25 °C on cooling from the respective isotropic liquids (crossed polarizers, magnification ×200).



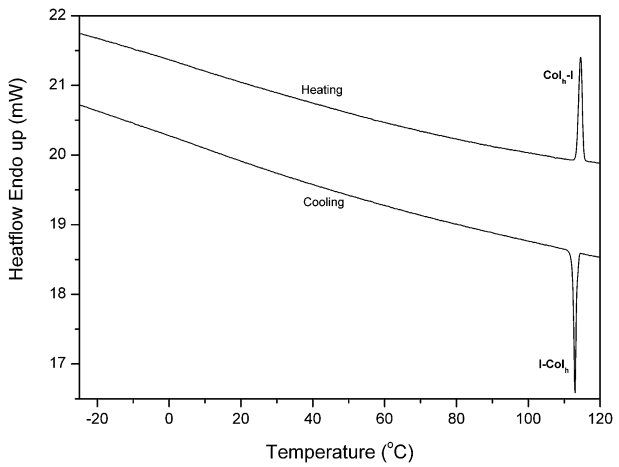



**Fig. 2** DSC thermogram of compound **5** on heating and cooling cycles (scan rate 5 °C min$^{-1}$).

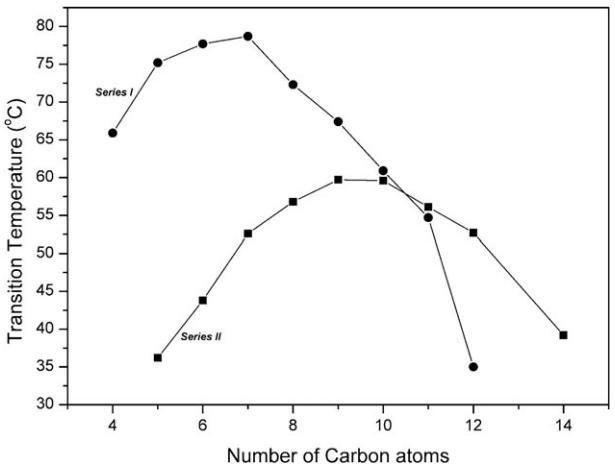



**Fig. 3** Variation of transition temperatures (Col$_h$–I) with number of carbon atoms in the *n*-alkyl chains.

columnar mesophase behavior at room temperature as is evident from a single thermal transition in their DSC thermograms while heating and cooling, which is assigned to columnar hexagonal to isotropic and isotropic to columnar hexagonal phase transitions, respectively. These compounds do not crystallize even after cooling to −30 °C. The compounds **4g–i** are crystalline at room temperature, **4g** upon heating passes to columnar phase at 37.6 °C and at 61 °C it clears to isotropic phase while cooling the mesophase transition is at 59 °C and the phase is stable down to room temperature and the sample does not crystallize. Compound **4h** exhibits similar behavior as that of **4a** whereas the compound **4i** shows a monotropic columnar hexagonal phase below 31 °C and crystallizes at 9 °C. In *Series II*, except for compounds **6a** and **6b** all the other compounds display columnar mesophases at room temperature and none of them show any sign of crystallization upon cooling to −30 °C as shown in Table 1. Compounds **6a** and **6b** are crystalline at room temperature and exhibit monotropic columnar hexagonal phases while cooling from the isotropic state similar to the compound **4i** but they do not crystallize immediately upon cooling to low temperature. So the compounds **4b–4f**, **5** and **6c–i** are truly room-temperature liquid crystals exhibiting only one columnar phase over a wide range of temperature. These compounds could be suitable electron transport candidates while considering the potential application of discotic liquid crystals for light emitting diodes and photovoltaic solar cells. The variation of transition temperatures ($T_{\text{Col-I}}$) and transition enthalpies ($\Delta H_{\text{Col-I}}$) with the number of carbon atoms in the normal alkoxy chains for the compounds of both the series are shown in Fig. 3 and 4, respectively. Both

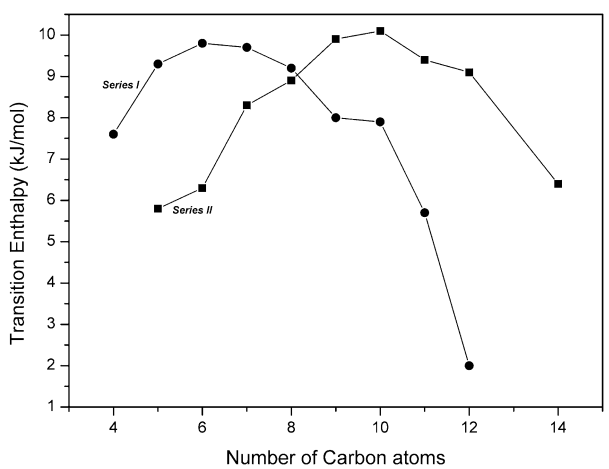



**Fig. 4** Variation of transition enthalpy $\Delta H$ (Col$_h$–I) with number of carbon atoms in the *n*-alkyl chains.

the transitional properties increase marginally as the number of carbon atoms increase and attain the maximum value about the middle of the series and then the values fall as the number of carbon atoms are further increased in the homologues series. The extent of order present in the mesophase is often characterized by the isotropization enthalpy and isotropization entropy. The branched alkyl chains exert two contrasting effects, one space-filling effect and the other is a steric effect. So depending on the balance of these competing factors the mesophase order may increase or decrease. Thus within a series, the mesophase order may vary in a non-liner fashion depending on the relative contributions of these competing factors for each member of the series. In addition, there is the rigidity of the *n*-alkyl chains which also contributes towards the order of the compounds, so also symmetry in terms of the alkyl chain lengths, whereas stereoheterogeneity of the branched chains contribute towards the mesophase disorder. So as we move towards longer chain lengths the molecules approach towards symmetry and then again deviate from symmetry in terms of alkyl chain lengths. Accordingly the order in the mesophase marginally increases, attains the maximum value and then decreases. It should be noted that the flexibility of the longer alkyl chains also contributes for the mesophase disorder in the higher members of the homologues series. In *Series II* since the molecules possess four branched alkyl chains the steric effect exerted by the branch points might dominate over the space-filling effect of the branch points and this could be the reason for lower clearing temperatures and higher fluidity of these compounds as compared to the members of *Series I*. The competition between steric effects and symmetric approach in the lower members of the *Series II* is just in favour of the latter so with increase in the chain length the stability of the mesophase increases, attains the maximum value and then decreases in the higher homologues where both steric effect of the branched alkyl chains and bending of the longer alkyl chains contribute for the mesophase disorder.

## X-Ray diffraction study

In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples taken in glass capillaries at room-temperature. The X-ray diffraction patterns of the mesophase exhibited by all the samples belonging to both the series is supportive of a discotic hexagonal columnar arrangement. As a typical example, the X-ray diffraction pattern of compound **4e** and the intensity *vs.* theta ($\theta$) plot derived from the pattern are shown in Fig. 5. Four sharp rings, one strong ($d_{10}$) and three weak reflections are seen in the pattern as well as in the plot in the small-angle region. Qualitatively all the compounds show similar X-ray diffraction patterns. The *d*-spacings of these four rings are in the ratio $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$ and they can be indexed as 10, 11, 20, 21 reflections of a two-dimensional hexagonal lattice. Additionally, a fairly narrow diffraction ring corresponding to a spacing of 3.7 Å, matching the interdisc (intracolumnar = $d_{01}$) spacing within a column, and a broad diffuse reflection at ~4.6 Å suggesting a liquid like structure of the alkyl chains, are also seen in the wide angle region. So the discotic molecules stack one on top of the other to form the columns and these columns in turn arrange themselves in two-dimensional hexagonal fashion for both series of compounds. In the columns the insulating alkyl chains surround the conducting aromatic cores because of nano phase-segregation. The intercolumnar distances calculated using the relation $d_{10}/\cos 30^\circ$ for all the compounds are listed in Table 2. In both the series it is evident that as '*n*' increases the diameter of the cylindrical columns formed by the discotic molecules also increases as shown in the Fig. 6. The intercolumnar distances varies from 20–26 Å where as the intracolumnar distance is around 3.7 Å which is usually observed for discotic columnar mesophases. Compound **5** also exhibits the same feature as described above but the intracolumnar core–core separation in this material is 3.43 Å and the peak is narrow and relatively strong at room temperature suggesting high intracolumnar order in this particular compound. This high intracolumnar order could be due to the added intermolecular interactions by two additional hydrogen bonded rings in the molecular core of compound **5**. The position of the peak $d_{01}$ ($d_{intra}$) is temperature dependent such that $d_{intra}$ increases on increasing the temperature. However, the core–core distance in compound **5** is 3.43 Å at 25 °C, whereas close to the isotropic temperature the core–core distance is 3.49 Å (105 °C) indicating relatively strong intracolumnar order in this compound. For other compounds which were investigated at higher temperatures it was found that the $d_{01}$ peaks become broader with increasing temperature, indicating a decrease in the degree of ordering along the columns. This observation may be interpreted on the basis that the average length of the order domains along the column decreases as the temperature is increased. Furthermore, increasing *n*, we note that the width of the (01) peak increases even at room temperature, suggesting the decrease in intracolumnar order with increasing the chain length around the discotic core. As can be seen from Fig. 6 the intercolumnar distances for both the series increase, as anticipated, with increase in the number of carbon atoms in the alkyl chains.

**Table 2** *d*-Spacings, intercolumnar ($d_{inter}$) and intracolumnar core–core distances ($d_{intra}$) for the mesophases of *Series I* and *Series II*, deduced from X-ray measurements at 25 °C

| Compound (*n*) | *d*-Spacing/Å | $d_{inter}$/Å | $d_{intra}$/Å |
|---|---|---|---|
| **4a** (4) | 17.5 | 20.2 | 3.65 |
| **4b** (5) | 18.2 | 21.0 | 3.69 |
| **4c** (6) | 19.0 | 21.9 | 3.64 |
| **4d** (7) | 19.7 | 22.7 | 3.66 |
| **4e** (8) | 20.3 | 23.4 | 3.67 |
| **4f** (9) | 20.9 | 24.0 | 3.67 |
| **4g** (10) | 21.3 | 24.6 | 3.69 |
| **4h** (11) | 22.0 | 25.3 | 3.68 |
| **4i** (12) | 22.6 | 26.1 | 3.69 |
| **5** | 19.4 | 22.4 | 3.43 |
| **6a** (5) | 19.6 | 22.6 | 3.68 |
| **6b** (6) | 19.9 | 22.9 | 3.69 |
| **6c** (7) | 20.1 | 23.2 | 3.69 |
| **6d** (8) | 20.5 | 23.7 | 3.69 |
| **6e** (9) | 21.0 | 24.2 | 3.69 |
| **6f** (10) | 21.3 | 24.6 | 3.69 |
| **6g** (11) | 21.5 | 24.8 | — |
| **6h** (12) | 21.8 | 25.1 | — |
| **6i** (14) | 22.3 | 25.7 | — |

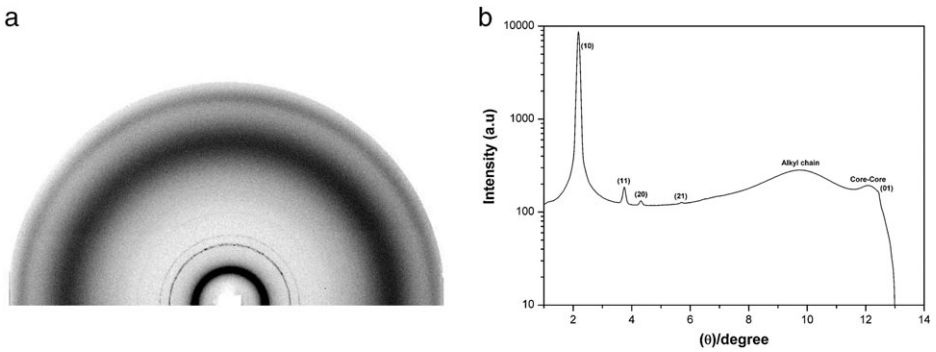



**Fig. 5** X-Ray diffraction pattern (a) and its derived intensity *vs.* $\theta$ plot (b) of the mesophase of compound **4e** recorded at 25 °C.



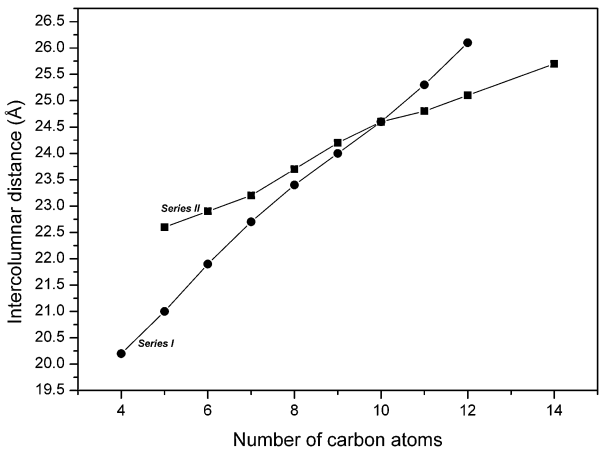



**Fig. 6** Variation of intercolumnar distances in both the series with number of carbon atoms in the *n*-alkyl chains.

From Fig. 6 it is very clear that the lower members of the *Series I* possess lower value of intercolumnar distances when compared with the corresponding members of the *Series II* but the trend reverses as the number of carbon atoms in the alkyl chains increases further. This could be because of the fact that in *Series I* the molecules contain four shorter *n*-alkyl chains and two longer alkyl (3,7-dimethyloctyl) chains so the effective diameter of the molecules are decided by the shorter chains whereas in *Series II* the molecules contain four longer alkyl (3,7-dimethyloctyl) chains and two shorter *n*-alkyl chains and hence the effective molecular diameter is decided by the longer chains which explains the difference of intercolumnar distances in the lower members. The situation is reversed in the higher members. Fig. 6 also reveals that *Series I* and *Series II* show different slopes. The reason for the difference in slopes may be due to the different positions of the *n*-alkyl chains in the molecules. For *Series I*, *n*-alkyls are outward pointing side-chains and the branched chains are lateral but the situation is reversed for *Series II*. The effective dimensions of both the series are mainly determined by the side chains rather than lateral chains which explain the difference in slopes. The bending of the longer alkyl chains, in part, will lead to a decrease of the core–core overlap between discs in the columns. Therefore the π–π interactions will be diminished and hence the $d_{01}$ peak broadens with increase in the number of carbon atoms in the alkyl chains. For compounds **6g–i** this peak is not discernable even after long exposure time, this could be because of the combined effect of the bending of the longer alkyl chains and the steric effect of the branched alkyl chains for the intracolumnar disorder.

## Conclusions

In conclusion, we have synthesized two novel series of rufigallol based room-temperature discotic liquid crystals with the help of microwave dielectric heating within a few minutes under mild basic conditions in very good yield. The columnar mesophase behavior of all the compounds has been investigated by polarizing optical microscopy and differential scanning calorimetry. The mesophase stability decreases as the length of the alkyl chain increases in both the series. All the compounds exhibit a columnar hexagonal mesophase over a broad range of temperature. The columnar hexagonal structure of the mesophase was established by X-ray diffraction studies. As anticipated, the intercolumnar distance increases with increase in the alkyl chain length in both the series. Compound **5** being a difunctional molecule can be used to prepare various discotic oligomers and polymers. These electron-deficient room-temperature discotic liquid crystals may find applications in light emitting diodes, photovoltaic solar cells, thin film transistors, *etc*. The measurement of electron mobility in some of these materials is in progress.

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