

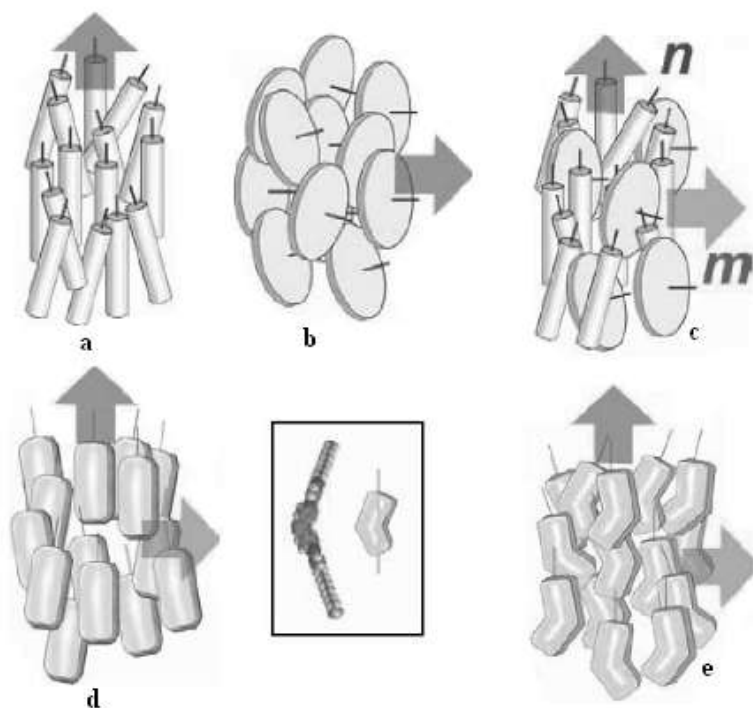
# CHAPTER 6

## Novel discotic-calamitic hybrids: synthesis and characterization of cyanobiphenyl substituted rufigallols

### 6.1 Introduction

One of the most active areas of research in liquid crystal science in recent years has been the search for the elusive biaxial nematic phase [1, 2], where the unique axes of the molecules arranged not only in a common direction (known as director) but also there is a correlation of the molecules in a direction perpendicular to the director (figure 1). The hunt for this new liquid crystal phase began more than 30 years ago, when it was recognized that the molecules forming liquid crystals deviate from their presumed cylindrical shape [3]. In fact, the molecules are more lozenge-like, and it is because of this lowering of the molecular symmetry that two nematic phases should be possible. Indeed, the first claimed discovery of a biaxial nematic [4] was for a compound formed of spoon-like molecules, and similar claims soon followed for cross-shaped [5] and bone-shaped molecules [6]. Till now, there have been many claims [7, 8] for its discovery in low molar mass thermotropic liquid crystals, although experimental difficulties in unambiguously identifying the symmetry of these phases raise questions concerning these assignments. Recently, a biaxial N phase was obtained in bent core thermotropic mesogens [9].

Theoretical studies and mean field calculations [10], have shown that the biaxial nematic phase ( $N_b$ ) is obtained by changing a shape biaxiality parameter ( $\eta$ ) between a rod at one extreme ( $\eta = 0$ ) and a disc ( $\eta = 1$ ) at the other. The  $N_b$  phase exists over ranges such as  $0.2 \leq \eta \leq 0.8$ , but is most stable at  $\eta = 0.4$ . Such a structure is then properly intermediate between a rod and a disc, and this led to proposals that the  $N_b$  phase might be realized in rod/disc mixtures.

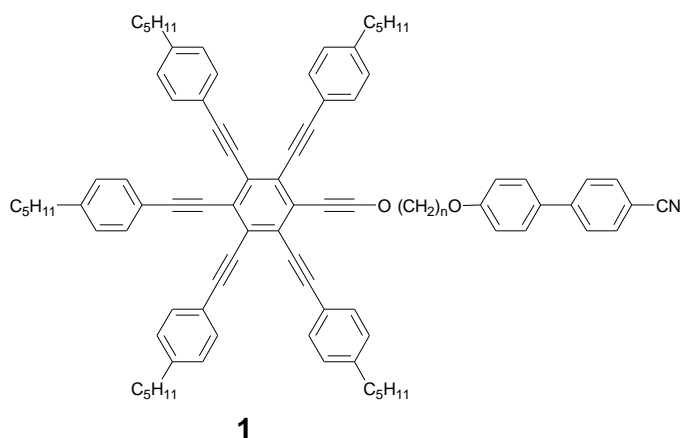


**Figure 1.** Schematic illustration of N phases with major  $n$  and minor  $m$  directors: (a) uniaxial N comprised of cylindrically symmetric mesogens (b) uniaxial discotic nematic (c) biaxial N phase by a mixture of rods and disks (d) biaxial nematic phase from anisotropic brick-like molecules (e) biaxial N phase of bent-core mesogens

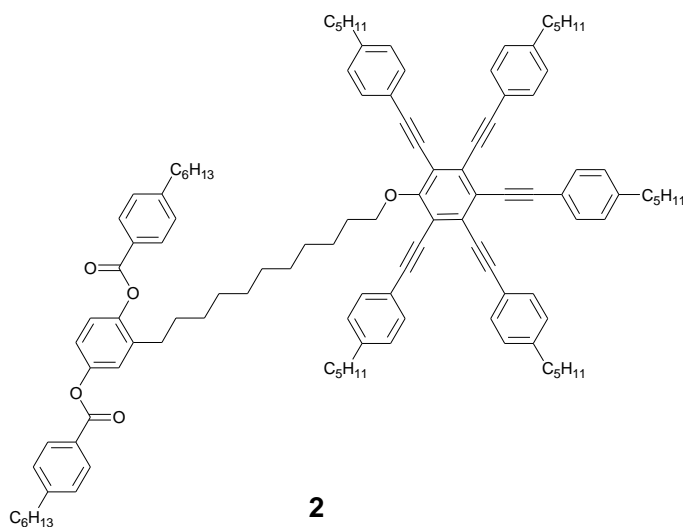
In such a mixture the optimum packing arrangement has the long axes of the rods arranged perpendicularly to the short axes of the discs and hence, the system has two directors. This idea was investigated in theoretical approaches to the biaxial nematic phase formed from binary mixtures of rod- and disc-like molecules [11]. The situation with respect to physical mixtures is not so straightforward because a mixture of rods and disc should [12], and indeed does [13], separate into two uniaxial nematic phases, one rich in rods and the other rich in discs. However, theoretical work by Sharma et al. [14] and by Vanakaras et al. [15] has shown that rod/disc

mixtures can lead to  $N_b$  phases if the rod and disc are attracted more to one another than to each other.

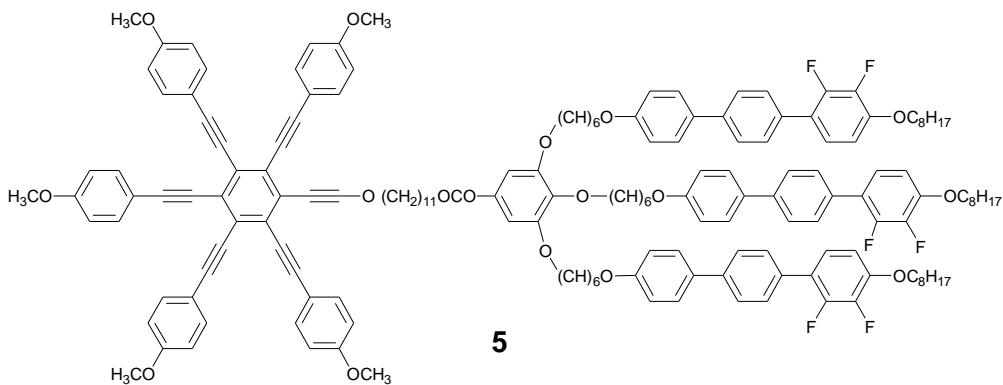
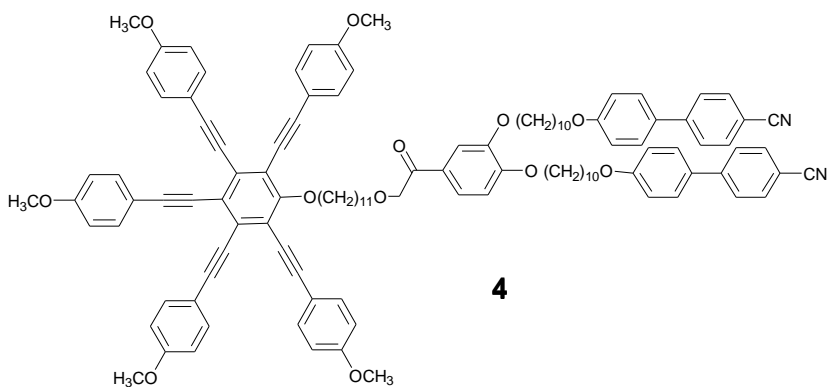
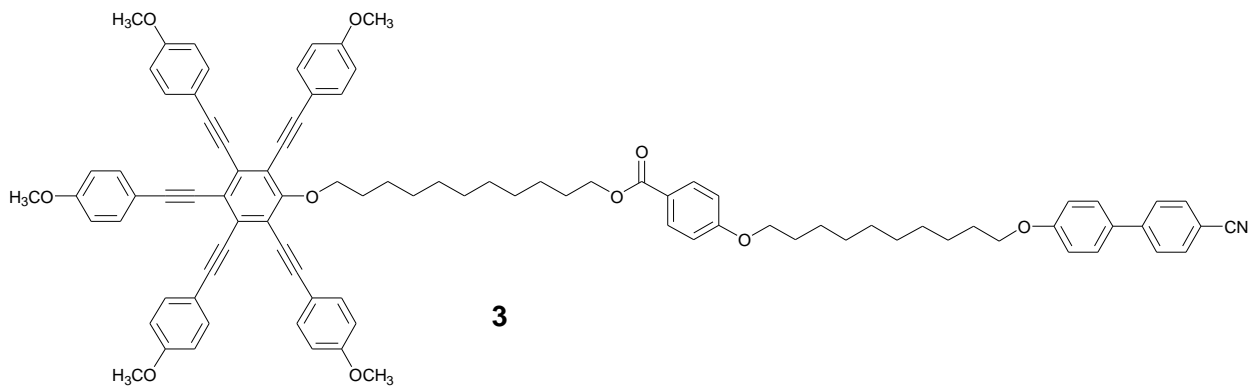
One way to overcome this problem is to attach rod-like and disc-like units covalently via flexible alkyl spacers, so that they could not phase separate. The reported molecular systems are the interconnection between a rod and a disc and such dimers have recently been the subject of computer simulation study [16]. For example, Luckhurst *et al.* synthesized the first rod-disc dimers (**1**) by joining together the disc-shaped [pentakis(4-pentylphenylethynyl)] benzene and the rod shaped 4-cyanobiphenyl moieties through an ether linkage [17].



Bruce *et al.* [18] examined the molecular biaxiality which contains a pentyne disc joined to the lateral rod-like molecules (**2**).

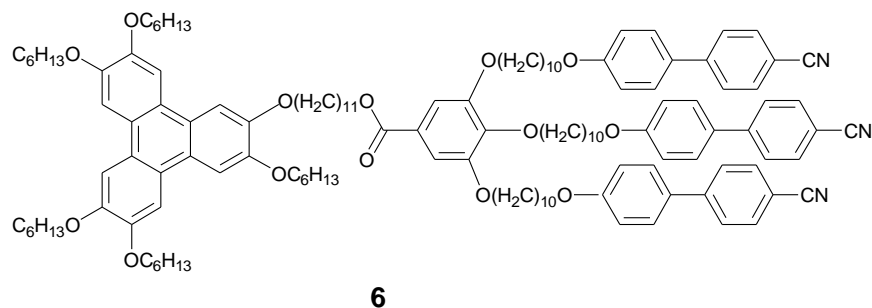


Mehl and coworkers [19] studied the miscibility of disc- and rod-shaped mesogens (**3**, **4**) in the N phase.



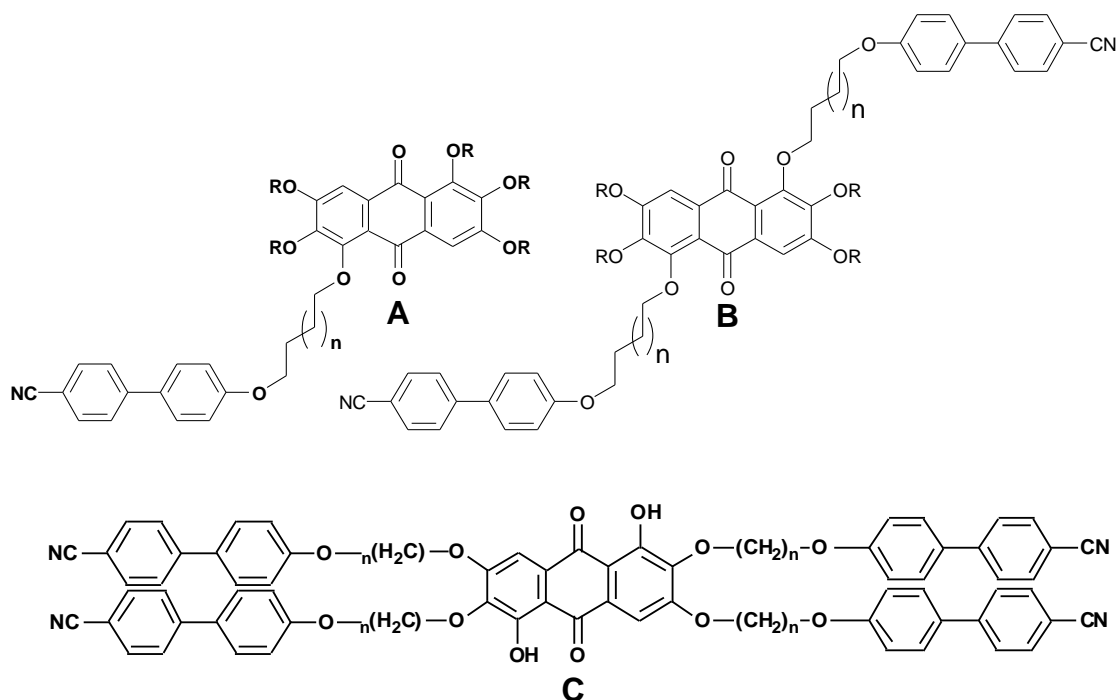
They also investigated multiple levels of order with N and several smectic phases in a material containing disc- and rod-like mesogenic units (**5**) [20].

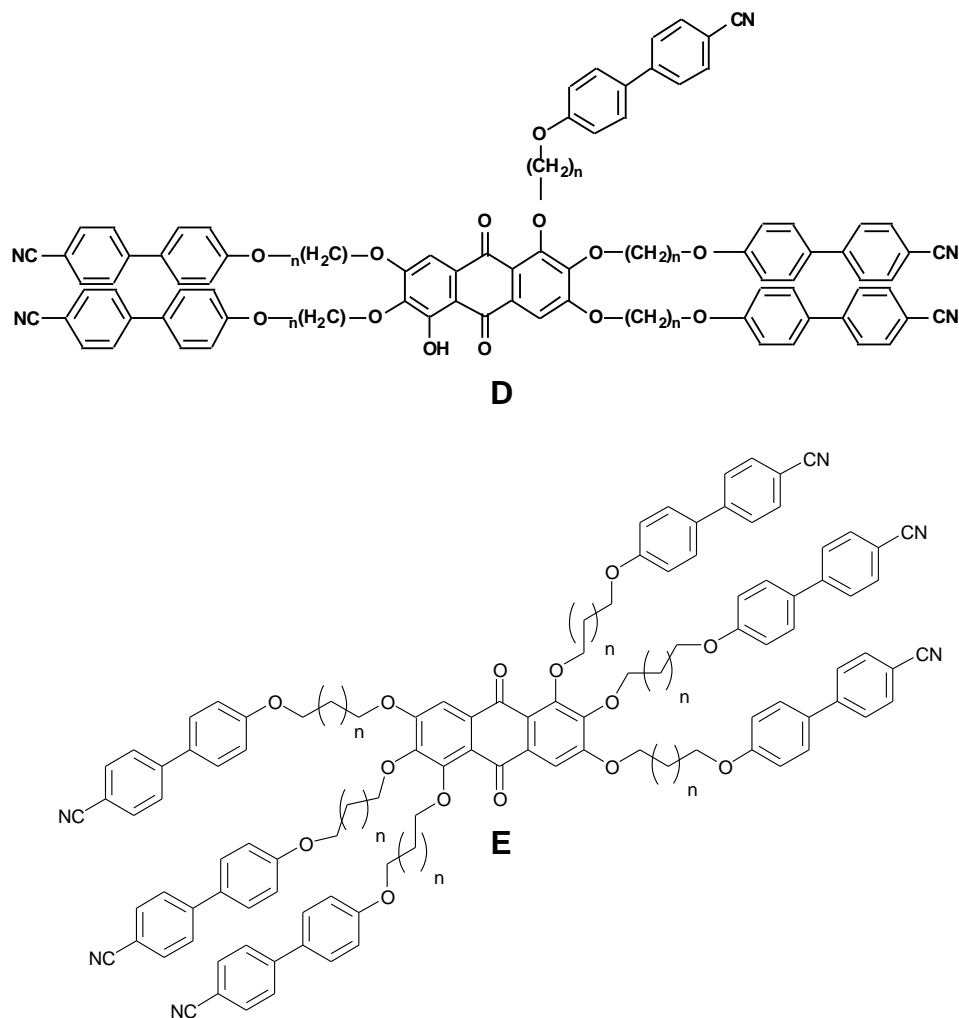
Recently, disc-shaped triphenylene moiety attached with three cyanobiphenyl units (**6**) has been reported [21] to form a thermodynamically stable layered phase.



## 6.2 Objective

In the molecular systems described above, one, two or three rods have been attached to a single disc like molecule to create  $N_b$  phase. We have extended this approach and prepared a series of novel molecules in which one, two, four, five, six rod-like 4-cyanobiphenyl moieties are attached to a central rufigallol core via flexible alkyl spacers (structures **A-E**, figure 2).



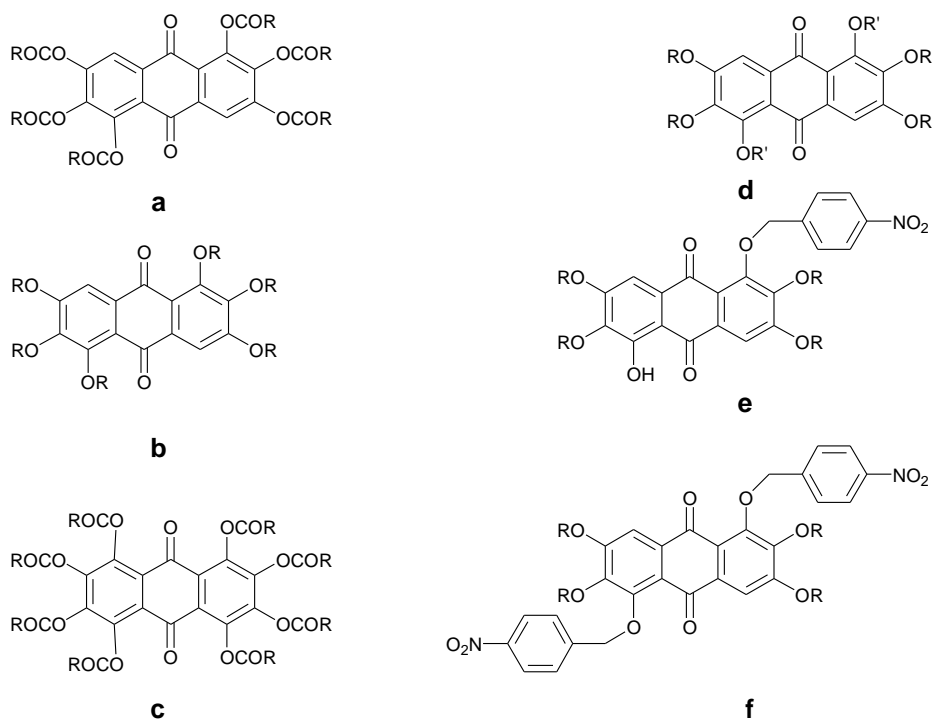


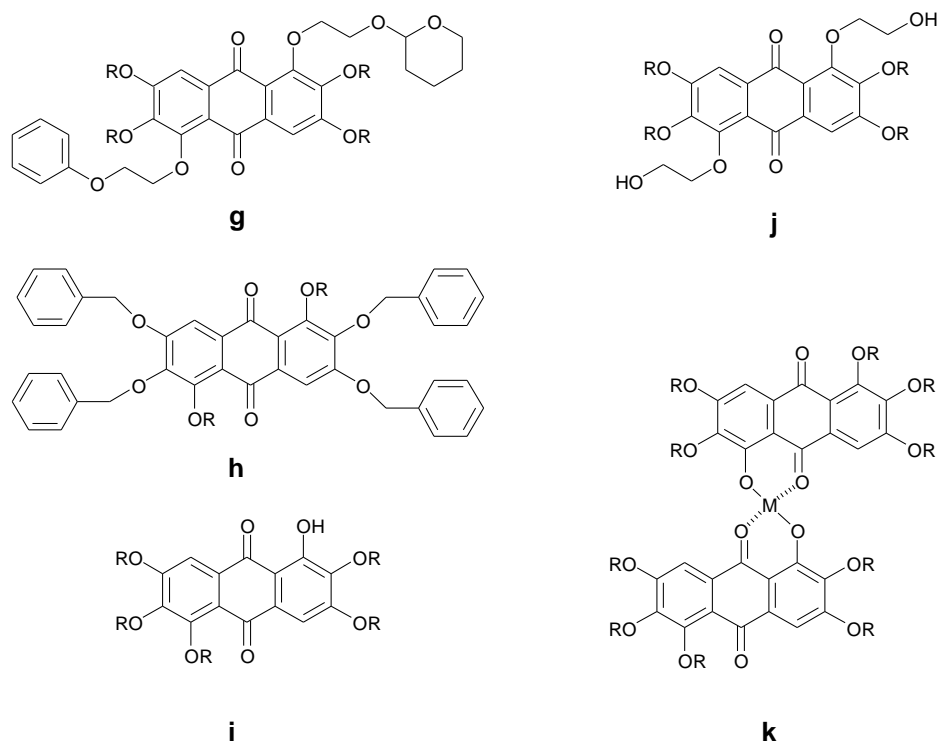
**Figure 2.** Molecular architecture for discotic-calamitic hybrids.

The rufigallol core was chosen because it is an elongated molecule with two-fold symmetry. It is known to promote liquid crystalline behaviour in a wide range of molecular architectures and has a very versatile synthetic chemistry [22]. Its several derivatives are known to display optically biaxial phases [23]. Therefore, the attachment of cyanobiphenyl groups around the periphery may lead to biaxial nematic phases.

### 6.3 Ruffigallol as a discotic core

1, 2, 3, 5, 6, 7-hexahydroxyanthraquinone (ruffigallol) derivatives are one of the earliest systems reported to form columnar mesophase. They are interesting materials as these molecules have an elongated core with a two-fold symmetry axis, they are coloured, they exhibit an important polymorphism, the core is electron-deficient in nature, they are thermally stable and their chemistry is fairly easy. Billard and co-workers reported the first discotic liquid crystalline hexaesters of ruffigallol in 1980 [24] and since then about 100 different discotic liquid crystalline derivatives of this molecule have been prepared and studied for various physical properties. These derivatives may be subdivided into following 11 structural types (figure 3). The chemistry and thermal behaviour of all these ruffigallol-based discotic liquid crystals has recently been described in a review article [22].





**Figure 3.** Rufigallol-based structures forming discotic liquid crystals.

#### 6.4 Synthesis of rufigallols

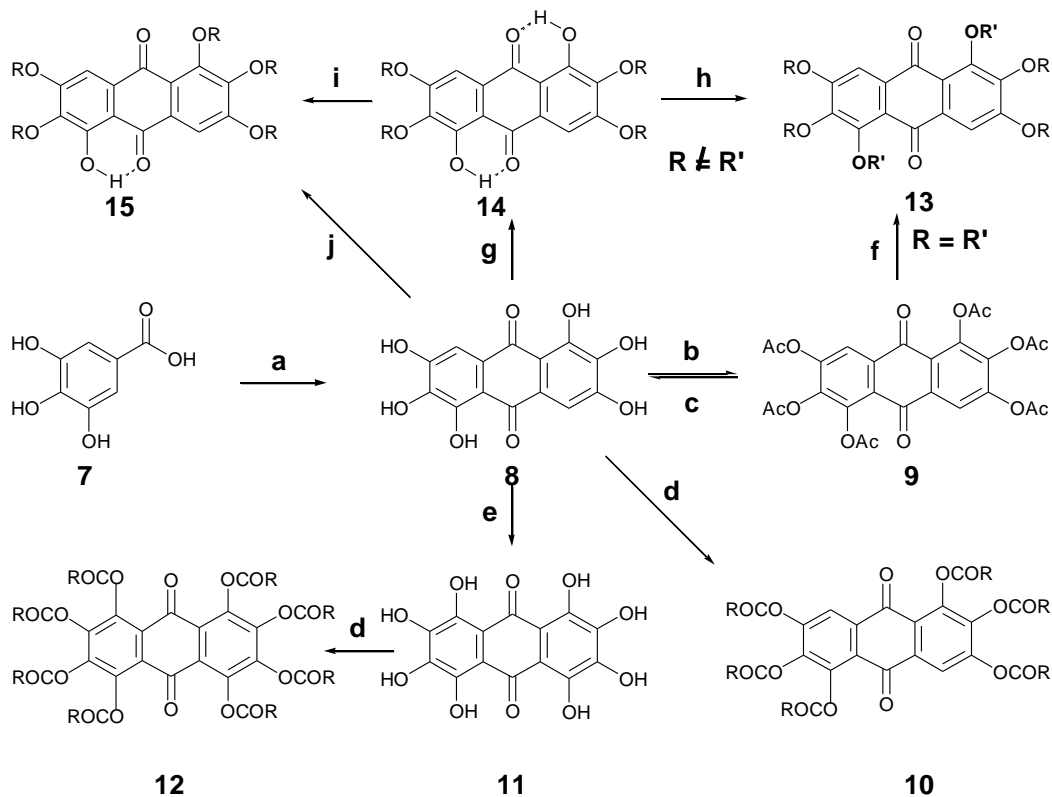
All the discotic liquid crystalline derivatives were essentially prepared from rufigallol (1,2,3,5,6,7-hexahydroxyanthraquinone). Acid-catalyzed self-condensation of gallic acid **7** yields crude rufigallol **8** which is normally purified through its hexa-acetate **9** (scheme 1) [24]. Pure rufigallol, obtained by the hydrolysis of hexa-acetate can be esterified with long-chain acid chlorides to get liquid crystalline hexaesters [25, 26]. Similarly, hexaethers can be prepared by the etherification of the hexaphenol but the ethers are better made directly from the hexaacetate [27].

The two hydroxyl groups at 1 and 5 positions in rufigallol are hydrogen bonded and, therefore, are less reactive. This unequal reactivity leads to the preparation of several unsymmetrical



rufigallol derivatives [28-33]. Further, as the two functional groups are readily available, main chain polymers of the tetraalkoxyrufigallol can be easily prepared [29].

Oxidation of 1,2,3,5,6,7-hexahydroxyanthraquinone yields octahydroxy-anthraquinone **11** (scheme 1) which on esterification with alkanoyl chlorides provides octa-substituted anthraquinone discotics [34].

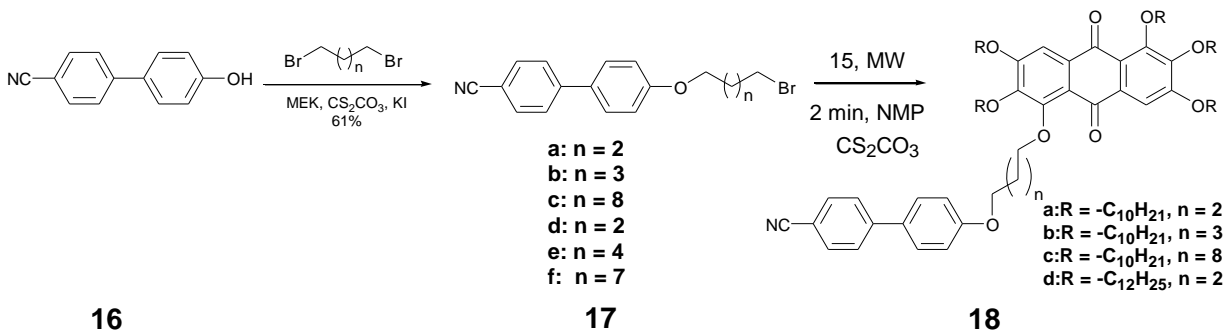


**Scheme 1.** (a)  $\text{H}_2\text{SO}_4$ , heat; (b)  $\text{Ac}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ; (c) Aq NaOH; (d) Py-acetone,  $\text{RCOCl}$ ; (e)  $\text{H}_3\text{BO}_3$ ,  $\text{HgO}$ ,  $\text{H}_2\text{SO}_4$ ; (f) DMF,  $\text{Na}_2\text{CO}_3$ ,  $\text{RBr}$ ,  $160^\circ\text{C}$ ; (g) DMSO, NaOH,  $\text{RBr}$ , TBAB,  $80^\circ\text{C}$ ; (h) DMF,  $\text{K}_2\text{CO}_3$ ,  $\text{RBr}$ , TBAB,  $\sim 100^\circ\text{C}$ ; (i) DMF,  $\text{Cs}_2\text{CO}_3$ ,  $\text{RBr}$ ; (j) ROH, TPP, DEAD.

### 6.5 Synthesis of rod-disc hybrids: mono alkoxyphenyl substituted rufigallols

The synthesis rod-disc monomer is outlined in scheme 2. Commercially available 4'-hydroxy-4-biphenylcarbonitrile **16** was alkylated under classical conditions with an excess of the

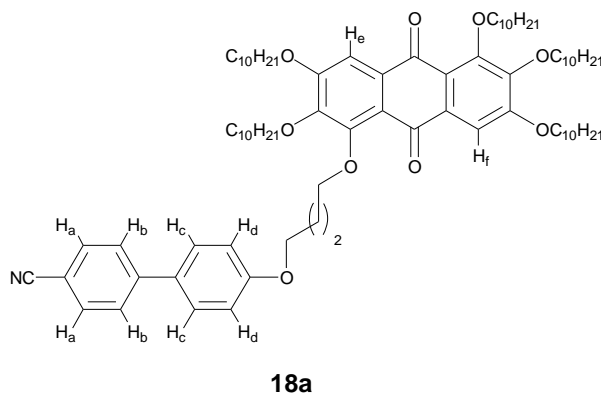
appropriate  $\alpha,\omega$ -dibromoalkane to obtain the  $\omega$ -brominated product **17** [35]. The bromo-terminated alkoxy cyanobiphenyls **17** was reacted with monohydroxyanthraquinone **15** under microwave heating to give the desired rod-disc dimers **18**. Thus, when 0.08 mmol of **17**, 0.12 mmol of **15** ( $R = -C_{10}H_{21}$ ) and  $CS_2CO_3$  as base in 0.5 ml of solvent was irradiated with 360W microwaves for 2 minutes, 40 mg of **18** formed.



**Scheme 2.** Synthesis of rod-disc dimers.

### 6.5.1 Characterization of discotic-calamitic dimers **18**

All the compounds were characterized from their  $^1H$  NMR, IR, UV-vis and elemental analyses. All the members of a series give similar spectra differing in only the number of alkyl chain  $CH_2$  protons. All Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. Figure 4 represents the  $^1H$  NMR spectrum of monocyanobiphenyl substituted rufigallol **18a**.



As expected from the above dimer structure, protons which are ortho to  $-\text{CN}$  group ( $\text{H}_a$ ) are in the same environment and therefore appear at the same  $\delta$  value. These protons couple with the neighboring  $\text{H}_b$  protons and appear as doublet (d) and vice-versa. As they are ( $\text{H}_a$ ,  $\text{H}_b$ ) attached to aromatic ring having strongly electron withdrawing  $-\text{CN}$  group they have  $\delta$  values higher compare to other hydrogens. Having ortho to  $-\text{CN}$  group  $\text{H}_a$  protons have highest  $\delta$  values ( $\delta = 7.7$ ) in comparison to  $\text{H}_b$  protons ( $\delta = 7.65$ ) and obviously, with respect to all other hydrogens. Similarly,  $\text{H}_c$  and  $\text{H}_d$  protons appear as doublet at  $\delta$  7.51 and 7.0 respectively. The two aromatic protons  $\text{H}_e$  and  $\text{H}_f$  in rufigallol moiety appear as two singlets with  $\delta$  values 7.6 and 7.58 respectively. The rufigallol  $-\text{OCH}_2$  appear at  $\delta$  4.15 as multiplates whereas  $-\text{OCH}_2$  attached to cyanobiphenyl moiety appear as triplets. Remaining aliphatic protons of the alkyl chains resonate between  $\delta$  0.8-2.1.

Figure 5 represents the IR spectrum of compound **18a**. It shows strong  $-\text{CN}$  peak at  $2225 \text{ cm}^{-1}$  and quinone carbonyl peak at  $1662 \text{ cm}^{-1}$ . Figure 6 represents the UV-Vis spectrum of **18a**, displaying absorption peaks at 287, 319 and 355 nm.

### 6.5.2 Thermal behaviour of discotic-calamitic dimers 18

The thermal behaviour of all the compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. The very first compound **18a**, prepared by the dimerization of rod-shaped cyanobiphenyl and disc-shaped rufigallol having four methylene units, showed columnar liquid crystalline property at room temperature. On heating, it transforms to the isotropic phase at about  $43 \text{ }^\circ\text{C}$ . On cooling a well defined texture (figure 7) of a columnar mesophase appeared at  $40.5 \text{ }^\circ\text{C}$  and remained down stable to room temperature. The DSC traces of compound **18a** obtained on heating and cooling runs are shown in figure 8. Interestingly,

increasing number of spacer length with same peripheral chain length in the rufigallol moiety destroys the liquid crystalline property of the material. For example, compound **18b** and **18c** with five and ten methylene units does not show any liquid crystalline phase. They melted at 65 °C and 55 °C respectively to the isotropic phase. On cooling they did not crystallize down to room temperature. Similarly, increasing number of atoms in the periphery also destabilized the columnar phase. Compound **18d** with twelve alkyl chains in the rufigallol moiety melted at 61.5 °C to the isotropic phase and did not solidify on further cooling. Data obtained from the heating and cooling cycles of DSC are collected in table 1. The peak temperatures are given in °C and the numbers in the parentheses indicate the transition enthalpy ( $\Delta H$ ) in  $\text{KJ mol}^{-1}$ .

**Table 1.** Phase transition temperatures (peak, °C) and associated enthalpy changes ( $\text{KJ mol}^{-1}$ , in parentheses) of rufigallol-based rod-disc dimers. Cr: Crystalline Phase;  $\text{Col}_h$ : Columnar hexagonal mesophase; I: Isotropic phase.

Compound	Heating scan	Cooling scan
<b>18a</b>	$\text{Col}_h$ 40 (3.1) I	I 38.6 (3) $\text{Col}_h$
<b>18b</b>	Cr 51(92) Cr 65 (37) I	-
<b>18c</b>	Cr 55 (72) I	-
<b>18d</b>	Cr 61.5 (56) I	-

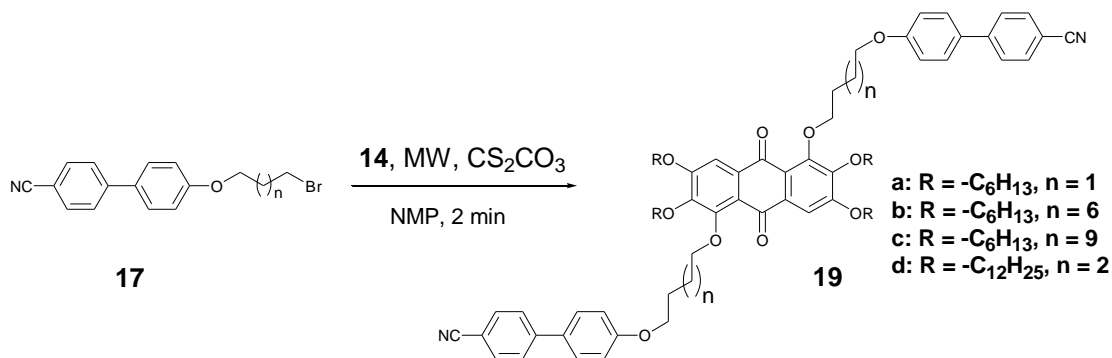
### 6.5.3 X-ray diffraction studies

The existence of the mesophase as a  $\text{Col}_h$  phase was confirmed from X-ray diffraction studies. The diffraction pattern was obtained at room temperature in the columnar phase for compound

**18a.** The X-ray diffraction pattern and one dimensional intensity versus  $2\theta$  profile are shown in figure 9. In the small angle region, three sharp peaks were observed, taken in the ascending order of the diffraction angle, the d spacing of the first reflection (lowest angle and highest intensity) to the other two is in the ratio of  $1:1/\sqrt{3}:1/\sqrt{4}$ . These values correspond to that expected from a two-dimensional hexagonal lattice. The d values are 2.15 nm, 1.242 nm and 1.067 nm. In the wide angle region there were two diffused peaks; a broad one at  $2\theta \sim 20^\circ$  and another relatively narrower peak at higher angles. The broad peak with a d-spacing of  $\sim 0.45$  nm was due to the liquid like packing of the aliphatic chains. The relatively narrow peak, which was separated from the broader one, corresponds to a spacing of 0.36 nm and was due to core-to-core (intracolumnar) separation. All the features fit into the well known model for the  $\text{Col}_h$  phase, in which the disc-like molecules stack one on top of another to form columns and the columns in turn are arranged in a two-dimensional hexagonal lattice. Within a column, the chains have only liquid-like correlations while the molecular core have a better positional order, albeit short-ranged, with an inter-core separation of 0.36 nm.

## 6.6 Synthesis of rod-disc-rod trimers: di-alkoxycyanobiphenyl substituted rufigallols

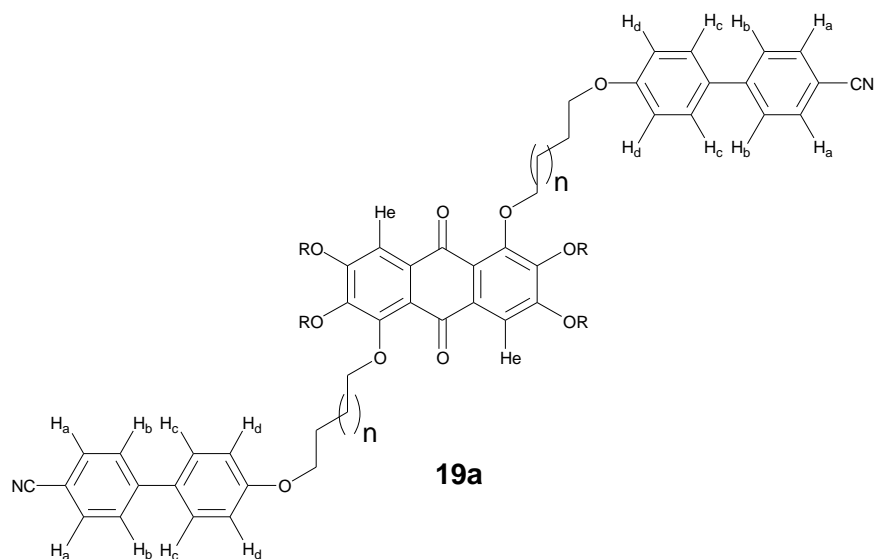
The synthesis of rod-disc-rod trimer is outlined in scheme 3. As discussed earlier, commercially available 4'-hydroxy-4-biphenylcarbonitrile was alkylated under classical reaction conditions with an excess of the appropriate  $\alpha, \omega$ -dibromoalkane to obtain the  $\omega$ -brominated product **17**. Bromo-terminated alkoxybiphenyl **17** was reacted with dihydroxy tetraalkoxy anthraquinone **14** under microwave heating in presence of cesium carbonate as base and NMP as solvent to give the desired trimer product within 2 minutes (**19**).



**Scheme 3.** Synthesis of rod-disc-rod trimers.

### 6.6.1 Characterization of rod-disc-rod trimers **19**

All the compounds were characterized from their <sup>1</sup>H NMR, IR, UV-vis and elemental analyses. All the members of a series give similar spectra differing in only the number of alkyl chain CH<sub>2</sub> protons. All Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. Figure 10 represents the <sup>1</sup>H NMR spectrum dialkoxycyanobiphenyl substituted rufigallol **19a**.



As expected from the above trimer structure, protons which are ortho to -CN group (H<sub>a</sub>) are in the same environment and therefore appear at the same δ value. These protons couple with

the neighboring H<sub>b</sub> protons and appear as doublet (d) and vice-versa. As they are (H<sub>a</sub>, H<sub>b</sub>) attached to aromatic ring having strongly electron withdrawing –CN group they have  $\delta$  values higher compare to other hydrogens. Having ortho to –CN group H<sub>a</sub> protons will have highest  $\delta$  values ( $\delta = 7.7$ ) in comparigion to H<sub>b</sub> protons ( $\delta = 7.65$ ) and obviously, with respect to all other hydrogens. Similarly H<sub>c</sub> and H<sub>d</sub> protons appear as doublet at  $\delta$  7.51 and 7.0, respectively. Due to symmetric nature of the molecules the two aromatic protons (H<sub>e</sub>) in the rufigallol moiety H<sub>e</sub> protons appear as singlet with a  $\delta$  value of 7.6. The rufigallol –OCH<sub>2</sub> and –OCH<sub>2</sub> attached to cyanobiphenyl moiety appear as triplets at  $\delta$  values 4.15 and 4.00 respectively. Remaining aliphatic protons of the alkyl chains resonate between  $\delta$  0.8-1.9.

Figure 11 represents the IR spectrum of compound **19a**. A strong peak at 2225 cm<sup>-1</sup> and 1664 cm<sup>-1</sup> represents –CN peak and quinone carbonyl peak, respectively.

Figure 12 represents the UV-Vis spectrum of **19a**. Its shows the absorption peaks at 287, 303, 351 nm. All the spectral data are in accordance with the structure.

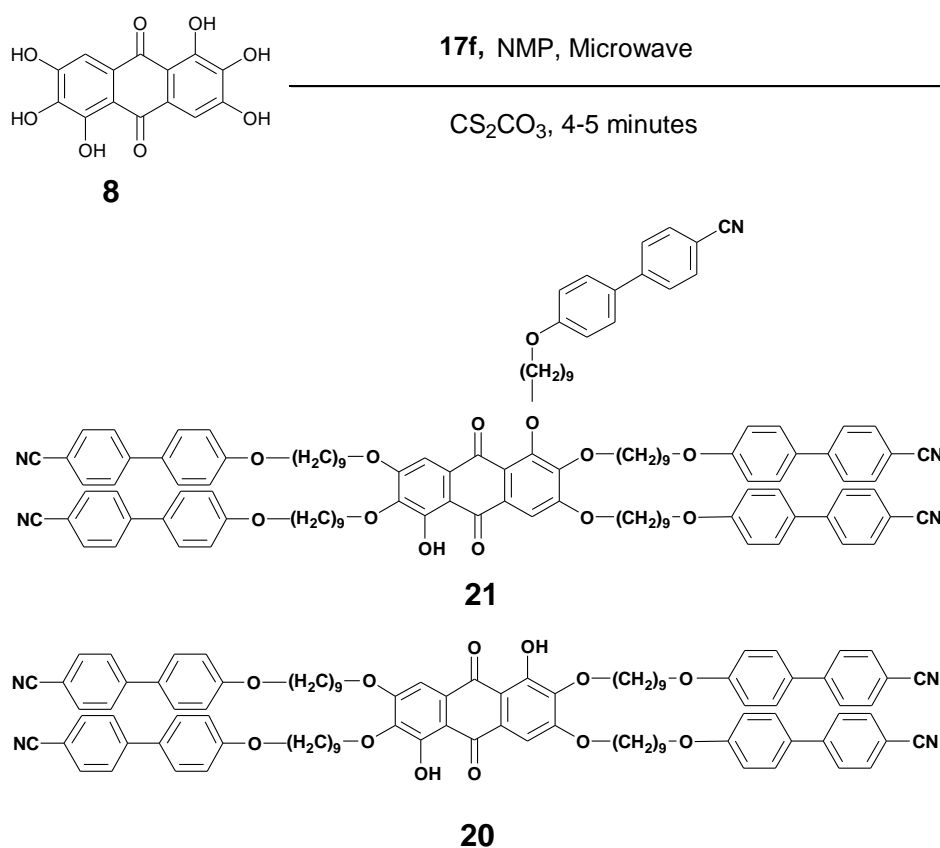
### 6.6.2 Thermal behavior of trimers 19

The thermal behavior of all the compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. Surprisingly, no member of this series showed liquid crystalline properties. They show only crystal to isotropic transition on heating and on cooling they did not crystallize upto room temperature.

### 6.7 Synthesis of pentamers: tetraalkoxycyanobiphenyl substituted rufigallols

The pentamer **20** has been prepared from hexahydroxyanthraquinone under microwave heating within 4-5 minutes (scheme 4). Thus rufigallol **8** dissolved in NMP, CS<sub>2</sub>CO<sub>3</sub> as a base and

bromoterminated alkoxybiphenyl (**17f**) mixed in a vial and subjected to microwave irradiation. Details of the procedure have been given in experimental section. It should be noted that attempted tetramerization under classical reaction conditions like DMSO, NaOH; DMSO, KOH; CS<sub>2</sub>CO<sub>3</sub>, DMF; K<sub>2</sub>CO<sub>3</sub>, DMF; CS<sub>2</sub>CO<sub>3</sub>, acetone; K<sub>2</sub>CO<sub>3</sub>, acetone; did not produce any desired product. Only microwave irradiation furnished 5-10% yield of the desired tetramer with a very little amount of hexamer **21**. While we managed to isolate pure pentamer **20** in low yield, hexamer **21** could not be isolated in absolute pure state by column chromatography.



**Scheme 4.** Synthesis of tetracyanobiphenyl substituted rufigallols.

### 6.7.1 Characterization

The pentamer was characterized from its <sup>1</sup>H NMR, IR, UV-vis and elemental analyses. All Spectral data and elemental analysis of the compound was in good agreement with its structure,



indicating the high purity the material. Figure 13 represents the  $^1\text{H}$  NMR spectrum tetraalkoxycyanobiphenyl substituted rufigallol **20**.

As expected, the OH proton signal appears at  $\delta$  12.7 while two aromatic protons resonate at  $\delta$  7.6. Because of the symmetric nature of the molecule the two aromatic hydrogens in rufigallol moiety appear as singlet. Ratio of the two aromatic hydroxyl groups and two aromatic protons are more or less same which indicate the formation of tetramer product. All other cyanobiphenyl hydrogens can be clearly seen in the NMR spectrum as discussed earlier. The  $-\text{OCH}_2$  hydrogens appear as multiplets at  $\delta$  3.9-4.3. Remaining aliphatic protons of the alkyl chains resonate between  $\delta$  0.8-1.9.

Figure 14 represents the IR spectrum of compound **20**. A strong peak at  $2223\text{ cm}^{-1}$  is due to  $-\text{CN}$  functional group from the cyanobiphenyl moiety.

Figure 15 represents the UV-Vis spectrum of **20**. Its shows absorption peaks at 287, 342, 429 nm. All the spectral data are in accordance with the structure.

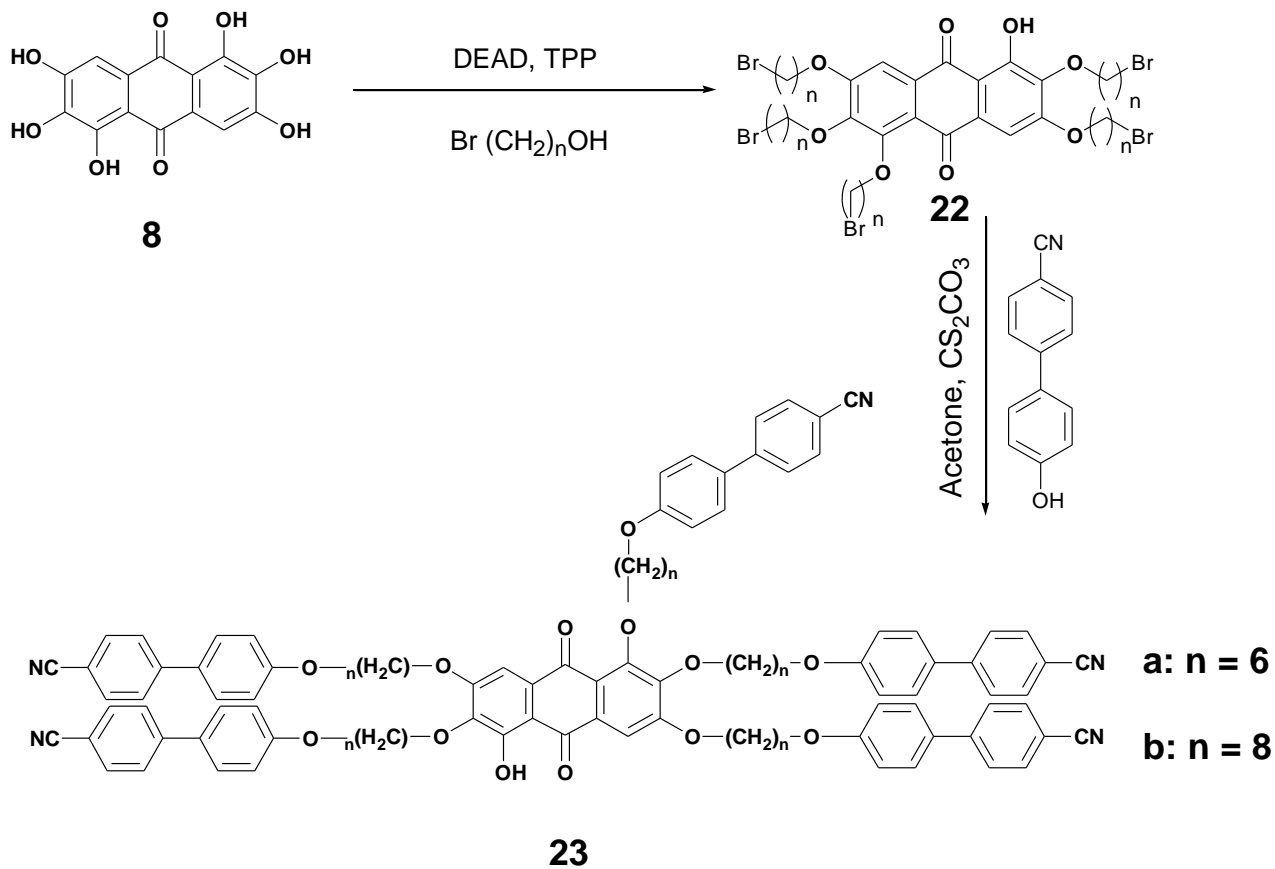
### 6.7.2 Thermal behaviour of **20**

The thermal behaviour of compound **20** was investigated by polarizing optical microscopy and differential scanning calorimetry. It shows enantiotropic nematic phase. On first heating the compound **20** melted at about  $85\text{ }^\circ\text{C}$  to the N phase which clears at about  $138\text{ }^\circ\text{C}$ . On cooling the N phase appears at  $137\text{ }^\circ\text{C}$  and it stays upto room temperature. However, the material could not deform at room temperature. Probably, it vitrified and formed a stable supercooled glassy N phase. The DSC traces of compound **20** obtained on heating and cooling runs are shown in figure 16. During the second heating, the mesophase to isotropic transition appeared at  $138\text{ }^\circ\text{C}$  with a heat of transition of  $2\text{ Jg}^{-1}$  indicating the mesophase to isotropic transition. On second cooling,

the isotropic phase to N phase again appeared at 137 °C and stable down to room temperature. The photomicrograph of the nematic phase is shown in figure 17.

### 6.8 Synthesis of hexamers: pentaalkoxycyanobiphenyl substituted rufigallols

One way to get ethers is mitsunobu reaction, where alcohol alcohol coupling occurs. When hexahydroxyanthraquinone **8** was reacted with bromo alcohols in presence of DEAD, TPP to get the corresponding ethers, exclusively pentasubstituted product **22** is formed as shown in Scheme 5. The corresponding pentasubstituted product on reaction with commercially available 4'-hydroxy-4-biphenylcarbonitrile **16** give the pentaalkoxycyanobiphenyl substituted rufigallols **23** in 15-20% yield.



**Scheme 5.** Synthesis of pentacyanobiphenyl substituted rufigallols.

### 6.8.1 Characterization

Both the hexamers were characterized from their  $^1\text{H}$  NMR, IR, UV-vis and elemental analyses. All Spectral data and elemental analysis of both the compounds were in good agreement with their structures, indicating the high purity of all the materials. Figure 18 represents the  $^1\text{H}$  NMR spectrum of pentacyanobiphenyl substituted rufigallol **23b**.

As expected, the OH proton signal appears at  $\delta$  12.7 while the two aromatic protons resonate at  $\delta$  7.4. Ten  $-\text{OCH}_2$  protons of the alkyl chains attached to rufigallol moiety give multiplates at  $\delta$  4.2. The  $-\text{OCH}_2$  protons attached to rod like cyanobiphenyl moiety also appear as multiplates at  $\delta$  4.0. All other cyanobiphenyl hydrogens can be clearly seen in the NMR spectrum as discussed earlier. Remaining aliphatic protons of the alkyl chains resonate between  $\delta$  1.4-2.1.

Figure 19 represents the IR spectrum of compound **23b**. A strong peak at  $2223\text{ cm}^{-1}$  is due to  $-\text{CN}$  functional group from the cyanobiphenyl moiety.

Figure 20 represents the UV-Vis spectrum of **23b**. It shows the absorption peaks at 280, 344, 432 nm. All the spectral data are in accordance with the structure.

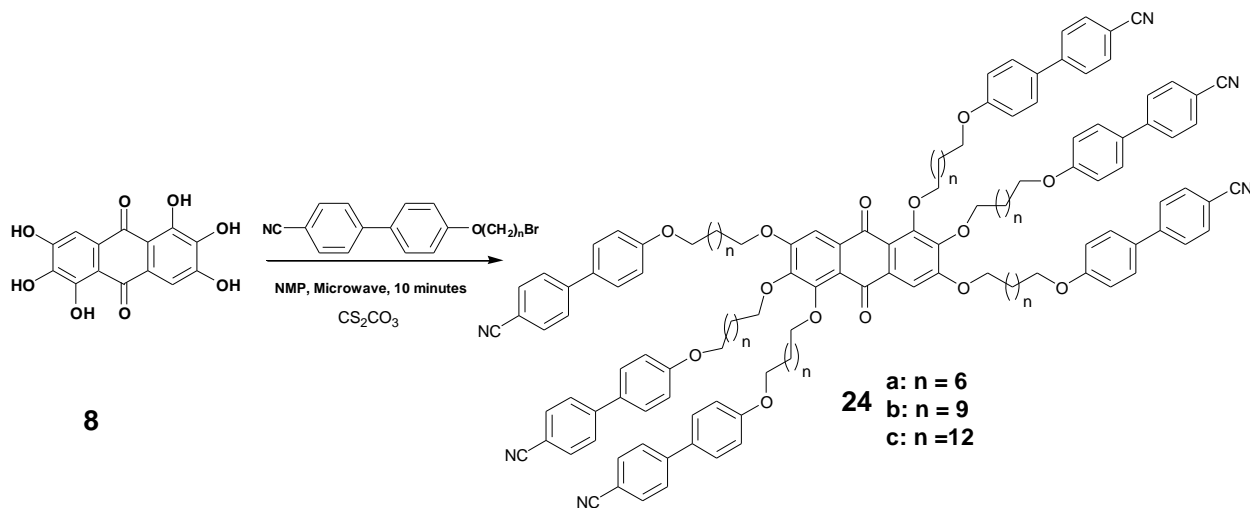
### 6.8.2 Thermal behaviour of 23

The thermal behaviour of compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. On heating, compound **23a** shows first a crystal to crystal transition at about  $127\text{ }^\circ\text{C}$ , then melts at  $143\text{ }^\circ\text{C}$  to the SmA phase which transforms to the nematic at about  $166\text{ }^\circ\text{C}$  and finally clears at  $187\text{ }^\circ\text{C}$ . The DSC of the first heating run is shown in figure 21. On cooling, the isotropic to nematic phase transition appears at  $185\text{ }^\circ\text{C}$  and the N-SmA transition at  $165\text{ }^\circ\text{C}$ . On continued cooling the material does not crystallize upto room

temperature. In the 2<sup>nd</sup> heating run no crystal to crystal transition peak is discernable. The photomicrograph of N and SmA phases are shown in figure 22 and 23, respectively. Similarly, compound **23b** melts to the SmA phase at 183 °C which transforms to a N phase at about 188 °C and finally clears at 203 °C. Before melting it also display two crystal to crystal transitions at about 160 °C and 173 °C. The DSC of the first heating run of compound **23b** is shown in figure 24. On cooling the isotropic phase, the N phase appears at about 201 °C and the N-SmA transition occurs at about 182 °C. Further cooling, the compound crystallizes at 148 °C. The N and SmA phases of the compound **23b** are shown in figure 25 and 26, respectively.

### 6.9 Synthesis of heptamer: hexaalkoxycyanobiphenyl substituted rufigallols

The synthesis of hexasubstituted rufigallol is outlined in scheme 6. Hexahydroxyanthraquinone **8**, with bromoterminated alkoxyphenyl **17** under microwave heating for 8-10 minutes (30s interval) give the desired hexaadduct **24**.



**Scheme 6.** Synthesis of hexacyanobiphenyl substituted rufigallols.

It should be noted that under classical condition, the reaction failed to produce any desired product. Rufigallol hexaacetate also under classical alkylation conditions did not produce any product.

### 6.9.1 Characterization of 24

All the heptamers with different chain lengths were characterized from their  $^1\text{H}$  NMR, IR, UV-vis and elemental analyses. All Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. Figure 27 represents the  $^1\text{H}$  NMR spectrum of hexacyanobiphenyl substituted rufigallol **24a**.

As expected, the -OH signal disappears, and all aromatic hydrogens attached to cyanobiphenyl moiety can be clearly seen in the spectrum as discussed earlier. The aromatic two hydrogens appear as singlet at  $\delta$  7.59. The  $-\text{OCH}_2$  protons appear as multiplates between  $\delta$  3.9-4.2. Remaining aliphatic protons of the alkyl chains resonate between  $\delta$  1.4-2.1.

Figure 28 represents the IR spectrum of compound **24a**. It shows strong  $-\text{CN}$  peak at  $2222\text{ cm}^{-1}$  and quinone carbonyl peak at  $1661\text{ cm}^{-1}$ .

Figure 29 represents the UV-Vis spectrum of **24a**. Its shows absorption peaks at 300 nm. All the spectral data are in accordance with the structure.

### 6.9.2 Thermal behaviour of 24

The thermal behaviour of compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. Compound **24a** showed only a monotropic nematic phase. The crystalline compound **24a** on heating melts at  $183\text{ }^\circ\text{C}$  to the isotropic phase. However, on cooling, the nematic phase appears at  $176\text{ }^\circ\text{C}$ , crystallizing at  $148\text{ }^\circ\text{C}$ . Under the microscope a

typical schlieren texture of the nematic phase is displayed, as shown in figure 30. Compound **24b** on heating melts at 94 °C to the SmA phase which transforms to the N phase at 116 °C and finally clears at 125 °C. Although its DSC trace shows only a single isotropic-nematic transition at 124 °C, POM reveals two other second order transitions. On cooling, the appearance of a SmA phase at 110 °C and a re-entrant nematic phase at 79 °C can be clearly seen under the POM. The photomicrograph of the N, SmA & re-entrant N phases are shown in figure 31(a-c). The DSC traces obtained on the heating and cooling runs are shown in figure 32. Compound **24c**, having longer spacer shows only monotropic SmA phase. On heating it melts at 143 °C to the isotropic phase. Before melting it also display two crystal to crystal transitions at about 85 °C and 115 °C. On cooling the SmA phase appears at 130 °C, which crystallizes at about 82 °C. The POM texture of the compound **24c** is shown in figure 33. Data obtained from the heating and cooling cycles of DSC are collected in table 2. The peak temperatures are given in °C and the numbers in the parentheses indicate the transition enthalpy ( $\Delta H$ ) in  $\text{KJ mol}^{-1}$ .

**Table 2.** Phase transition temperatures (peak, °C) and associated enthalpy changes ( $\text{KJ mol}^{-1}$ , in parenthesis) of rufigallol-based rod-disc mesogens

Compound	Heating scan	Cooling scan
<b>24a</b>	Cr 183 (126) I	I 126 (7) N 148 (88) Cr
<b>24b</b>	Cr 94 (81) SmA 116 <sup>a</sup> N 125 I	I 124 (7) N 110 <sup>a</sup> SmA 79 <sup>a</sup> N
<b>24c</b>	Cr 85 (27) Cr 115 (49) Cr 143 (141) I	I 130 (24) SmA 82 (49) Cr

<sup>a</sup> From POM ; Cr : Crystalline phase ; SmA : smectic A phase ; N : nematic phase.

## 6.10 Conclusion

The synthesis of several mesogenic rod-disc hybrids based on electron deficient anthraquinone core has been described in this chapter. We see there is actually a very critical balance to show mesomorphism in case of rod-disc dimer. All the rod-disc-rod trimers were found to be non-liquid crystalline. Between, pentamer and hexamer, the former shows only N phase, whereas the later one shows as both N and SmA phase. The combination of rod-disc-like moieties in the AQ (*n*CB)<sub>6</sub> series has perturbed the average molecular shape to yield calamitic mesophases. The average molecular shape is not disc-like in these homologues. It indicates that rod-like units in the tail have significantly changed the overall shape so that their thermal and orientational fluctuations inhibit the molecular packing required to observe the columnar mesophase. To our knowledge only three compounds were reported where six rod-like moieties have been attached to a discotic core. Shimizu *et al.* [36] reported a compound containing a triphenylene core attached to which were six azobenzene-based mesogens. In this system the length of the terminal chains on each rod-like mesogen considerably exceeded that of the spacer connecting the rod and disc. Rahman *et al.* [37] described the properties of a triphenylene-based compound containing six nitroazobenzene units attached via hexamethylene spacers. This compound exhibited a N phase and the authors considered that the triphenylene moiety acted only as a linking unit connecting the rod-like groups rather than a disc-like unit which would promote columnar phase formation. Imrie *et al.* [38] recently reported oligomeric discotic nematic liquid crystals consisting of a triphenylene core attached to which six cyanibiphenyl units via flexible alkyl spacers. By comparison, we have shown that the molecules are indeed rod-like in shape although they are derived from well known rufigallol discotic core. This behaviour has been interpreted in terms of the formation of rod-like structures by these supermolecules, [39] indicating that the

central units in these structures do not control the average molecular shape. Similar behaviour has been observed with comparable number of cyanobiphenyl units attached to a central unit for example substituted siloxysilanes [40] or functionalized fullerenes [41].

## 6.11 Experimental

General experimental conditions have been described in chapter 2.

### 6.11.1 Synthesis of 1,2,3,5,6,7-hexahydroxyanthraquinone (8) (rufigallol)

Rufigallol is prepared following the reported procedure [24]. A mixture of gallic acid (20 g) and conc.  $\text{H}_2\text{SO}_4$  (60 ml) was heated with stirring at 100 °C for 2h. The reaction mixture was cooled and poured over crushed ice and the orange precipitate obtained was filtered and washed with cold water, dried under high vacuum to get crude rufigallol as a brown solid (8 g, 49 %). The crude rufigallol was used in the subsequent steps without any further purification.

### 6.11.2 Synthesis of 1,5-Dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone (14): General Procedure.

All the tetraether were prepared following the reported procedure [28]. To a stirred solution of NaOH (4 eq.) in dry DMSO (50 ml) added crude rufigallol (5 g, 0.164 mmol) and 1-bromoalkane (4.4 eq.), and the mixture was heated to 70 °C and held at the same temperature under  $\text{N}_2$  for 18h. The reaction mixture was cooled, diluted with aq. HCl and extracted with chloroform (80 ml X 5). The combined chloroform extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Product was crystallized from EtOH: $\text{CHCl}_3$  (4:6). Yield 45 % (yellow solid).



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): All the compounds give similar spectra differing in only the number of alkyl chain CH<sub>2</sub> protons. δ 12.8 (s, 2H), 7.4 (s, 2H), 4.1 (t, 6.5, 8H), 1.9-1.7 (m, alkyl chain CH<sub>2</sub>), 1.0 (t, 12H).

### 6.11.3 Preparation of mono-hydroxy functionalized rufigallols (**15**)

To a solution of compound **14** (1 mmol) in dry DMF, was added Cs<sub>2</sub>CO<sub>3</sub> (1.2 mmol) and alkyl bromide (1.2 mmol). The reaction mixture was heated at 100 °C for 20h under an atmosphere of nitrogen. The mixture was then cooled to room temperature, water was added and the mixture extracted with chloroform. The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum. The dried crude product was acetylated by refluxing in acetic anhydride and pyridine for 18 hours under N<sub>2</sub>. The cooled reaction mixture was poured into ice, acidified with 5 % HCl and extracted with diethyl ether. The combined extracts were washed with water and brine and dried over anhydrous sodium sulphate. The dried crude organic phase was purified by column chromatography over silica gel. Chromatographic separation mainly gives two products; hexaalkoxyanthraquinone in about 60% yield and pentaalkoxy-monoacetoxyanthraquinone in about 30 % yield.

Pure monoacetates were hydrolyzed by refluxing for about one hour in ethanol containing 5 % aqueous NaOH. All the compounds were purified by repeated column chromatography. Pale yellow solid or semisolid materials were obtained upon the addition of ethyl alcohol to the ethereal solution of pure material (**15**). They were filtered, washed with ethyl alcohol and dried under vacuum.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): All the compounds give similar spectra differing in only the number of alkyl chain CH<sub>2</sub> protons. δ 12.66 (s, 1H), 7.64 (s, 1H), 7.38 (s, 1H), 4.08 (m, 10H), 1.87-1.26 (m, alkyl chain CH<sub>2</sub>), 1.07-0.88 (m, 15H).

#### 6.11.4 Synthetic procedure of rod-disc dimers (18)

In a typical reaction, **15** (R = -C<sub>6</sub>H<sub>13</sub>, 75 mg, 0.12 mmol), **17a** (26 mg, 0.08 mmol), Cs<sub>2</sub>CO<sub>3</sub> (39 mg, 0.12 mmol) were mixed in 1-methyl-2-pyrilidinone (0.4 ml) in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 2 min (30s X 4). The vial was taken out and water (10 ml) was added. Then the mixture extracted with dichloromethane (3 X 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography using 2 % ethyl acetate in petroleum ether as eluent to afford **18a** (40 mg, 80 %).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): All the compounds give similar spectra differing in only the number of alkyl chain CH<sub>2</sub> protons: δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.62 (s, 1H), 7.61 (s, 1H), 7.0 (d, *J* = 8.6 Hz, 2H), 4.15 (m, 12H), 4.05 (t, 2H), 0.8-2.1 (m, alkyl chain carbons).

**Elemental analysis:** Calculated for (**18a**) C<sub>81</sub>H<sub>123</sub>NO<sub>9</sub>: C 77.53, H 9.88, N 1.12 %; found C 77.20, H 9.85, N 1.03 %.

**IR data:** (The same spectrum is obtained for all the compounds **18a-d**):  $\nu_{\max}/\text{cm}^{-1}$  2922, 2850, 2225, 1662, 1604, 1465, 1330, 1265, 1137, 1029, 821, 721, 669.

**UV-Vis data:** all samples were measured in dichloromethane and similar spectrum is observed for all the compounds.  $\lambda_{\max}/\text{nm}$  287.6, 319.2.

### 6.11.5 Synthetic procedure of dialkoxyacyanobiphenyl substituted rufigallols (**19**)

In a typical reaction, **14** (R = -C<sub>6</sub>H<sub>13</sub>, 40 mg, 0.04 mmol), **17a** (154 mg, 0.468 mmol), Cs<sub>2</sub>CO<sub>3</sub> (152 mg, 0.47 mmol) were mixed in 1-methyl-2-pyrilidinone (0.4 ml) in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 2 min (30s X 4). The vial was taken out and water (10 ml) was added. Then the mixture extracted with dichloromethane (3 X 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography using 2% ethyl acetate in petroleum ether as eluent to afford **19a** (100 mg, 75 %).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): All the compounds give similar spectra differing in only the number of alkyl chain CH<sub>2</sub> protons: δ 7.69 (d, *J* = 8.2 Hz, 4H), 7.64 (d, *J* = 8.2 Hz, 4H), 7.52 (d, *J* = 8.6 Hz, 4H), 7.60 (s, 2H), 7.0 (d, *J* = 8.6 Hz, 4H), 4.15 (m, 12H), 4.05 (t, 2H), 0.8-1.9 (m, alkyl chain carbons).

**Elemental analysis:** Calculated for (**19a**) C<sub>72</sub>H<sub>86</sub>N<sub>2</sub>O<sub>10</sub>: C 75.89, H 7.61, N 2.46 %; found C 76.2, H 7.60, N 2.03 %.

**IR data:** (The same spectrum is obtained for all the compounds **19a-d**): ν<sub>max</sub>/cm<sup>-1</sup> 2931, 2225, 1664, 1602, 1569, 1496, 1467, 1326, 1267, 1130, 1184, 825.

**UV-Vis data:** All samples were measured in dichloromethane and similar spectrum is observed for all the compounds. λ<sub>max</sub>/nm 287.6, 303.6.

### 6.11.6 Synthetic procedure of tetraalkoxycyanobiphenyl substituted rufigallols (20)

In a typical reaction, **8** (30 mg, 0.09 mmol), cyanobiphenyl bromide **17f** (236 mg, 0.59 mmol), Cs<sub>2</sub>CO<sub>3</sub> (774 mg, 2.4 mmol) were mixed in 1-methyl-2-pyrilidinone (0.4 ml) in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 4 min (30s X 8). The vial was taken out and water (10 ml) was added. Then the mixture extracted with dichloromethane (3 X 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography (230-400 mesh) using 1:1 dichloromethane:petroleum ether as an eluent to afford **20** (15 mg, 10 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 12.7 (s, 2H), 7.69 (d, *J* = 8.2 Hz, 8H), 7.62 (d, *J* = 8.2 Hz, 8H), 7.50 (d, *J* = 8.6 Hz, 8H), 7.37 (s, 2H), 6.95 (d, 8.6 Hz, 8H), 3.9-4.3 (m, 16H), 0.8-1.9 (m, 54H).

**Elemental analysis:** Calculated for (**20**) C<sub>101</sub>H<sub>106</sub>N<sub>4</sub>O<sub>12</sub>: C 77.37, H 6.81, N 3.57 %; found C 77.2, H 7.10, N 3.51 %.

**IR data:** ν<sub>max</sub>/cm<sup>-1</sup> 3430, 2923, 2223, 1604, 1494, 1338, 1282, 1139, 1035, 823, 532.

**UV-Vis data:** λ<sub>max</sub>/nm 286, 320.

### 6.11.7 Synthetic procedure of pentaalkoxycyanobiphenyl substituted rufigallols (23)

Synthesis of **22**: Compound **8** (100 mg, 0.329 mmol), Br(CH<sub>2</sub>)<sub>8</sub>OH (453 mg, 2.5 mmol), triphenylphosphine (TPP, 569 mg, 2.16 mmol) and dichloromethane (20 ml) were mixed in a 100 ml two necked r. b flask and cooled in ice bath for 20 minutes. After keeping in ice-bath for 20 minutes DEAD (377 mg, 2.17 mmol) was added dropwise during 1 hour under nitrogen. The mixture was stirred overnight under nitrogen atmosphere. After the reaction is over the mixture

was evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography using 2-5 % ethyl acetate in petroleum ether as eluent to afford **22a** (150 mg, 41 %).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 12.8 (s, 1H), 7.40 (s, 2H), 4.2 (m, 10H), 3.5 (m, 12H), 1.5-2.0 (m, 38H).

**Elemental analysis:** Calculated for (**22a**) C<sub>44</sub>H<sub>63</sub>Br<sub>5</sub>O<sub>8</sub>: C 47.21, H 5.67 %; found C 46.9, H 5.60 %.

**IR data:** (The same spectrum is obtained for all the compounds **22a-b**):  $\nu_{\max}/\text{cm}^{-1}$  2935, 1768, 1662, 1602, 1425, 1363, 1278, 1137, 1095, 1033, 948, 794.

**UV-Vis data:**  $\lambda_{\max}/\text{nm}$  278.4, 287.2, 339.6, 424.8.

**Synthesis of 23a:** As an example the general synthesis of **23a** is described. In a round-bottom flask, 0.1 g of compound **22a** was dissolved in 15 ml of methyl ethyl ketone. To this, 4'-hydroxy-4-cyanobiphenyl (104 mg, 0.53 mmol), Cs<sub>2</sub>CO<sub>3</sub> (349 mg, 1 mmol) was added and the mixture was heated at 80°C for 16 hours under nitrogen with stirring. Then the mixture extracted with dichloromethane (3 X 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography (230-400 mesh) using 1:1 dichloromethane:petroleum ether as an eluent to afford **23a** (20 mg, 14 %).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 12.7 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 10H), 7.65 (d, *J* = 8.2 Hz, 10H), 7.62 (d, *J* = 8.6 Hz, 10H), 7.41 (s, 2H), 6.95 (d, 8.6 Hz, 10H), 4.15 (m, 10H), 4.0 (m, 10H), 1.0-2.0 (m, 40H).

**Elemental analysis:** Calculated for (**23a**) C<sub>109</sub>H<sub>103</sub>N<sub>5</sub>O<sub>13</sub>: C 77.44, H 6.09, N 4.14 %; found C 76.99, H 6.01, N 4.15 %.

**IR data:** (The same spectrum is obtained for all the compounds **23a-b**):  $\nu_{\max}/\text{cm}^{-1}$  3058, 2923, 2223, 1604, 1494, 1338, 1282, 1139, 1095, 1035, 823.

**UV-Vis data:**  $\lambda_{\max}/\text{nm}$  288, 344, 432.8.

#### 6.11.8 Synthetic procedure of hexacyanobiphenyl substituted rufigallols (**24**)

In a typical reaction, **8** (100 mg, 0.32 mmol), bromo terminated alkoxybiphenyl **17e** (1.4 g, 3.9 mol),  $\text{Cs}_2\text{CO}_3$  (1.3 g, 3.9 mol) were mixed in 1-methyl-2-pyrrolidinone (0.4 ml) in a small glass vial and loosely covered with a rubber septum. The mixture was heated in an unmodified household microwave oven at 360 W for 10 min (30s X 20). The vial was taken out and water (10 ml) was added. Then the mixture extracted with dichloromethane (3 X 10 ml). The combined organic extracts were washed with distilled water, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was then passed through a small column chromatography using 1:1 dichloromethane:petroleum ether as an eluent to afford **24a** (300 mg, 46 %).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ): 7.69 (d,  $J = 8.2$  Hz, 12H), 7.65 (d,  $J = 8.2$  Hz, 12H), 7.59 (s, 2H), 7.45 (d,  $J = 8.6$  Hz, 12H), 6.95 (d, 8.6 Hz, 12H), 3.95-4.25 (m, 24H), 1.4-2.1 (m, 48H).

**Elemental analysis:** Calculated for (**24a**)  $\text{C}_{128}\text{H}_{122}\text{N}_6\text{O}_{14}$ : C 78.10, H 6.25, N 4.24 %; found C 77.99, H 6.01, N 4.15 %.

**IR data:** (The same spectrum is obtained for all the compounds **24a-c**):  $\nu_{\max}/\text{cm}^{-1}$  2939, 2221, 1660, 1602, 1568, 1494, 1465, 1315, 1290, 1178, 1128, 997, 821.

**UV-Vis data:**  $\lambda_{\max}/\text{nm}$  300.

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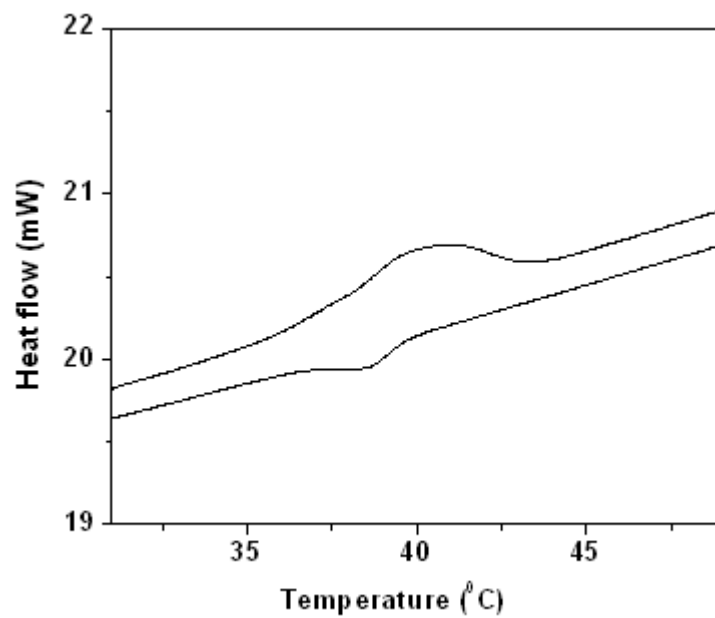




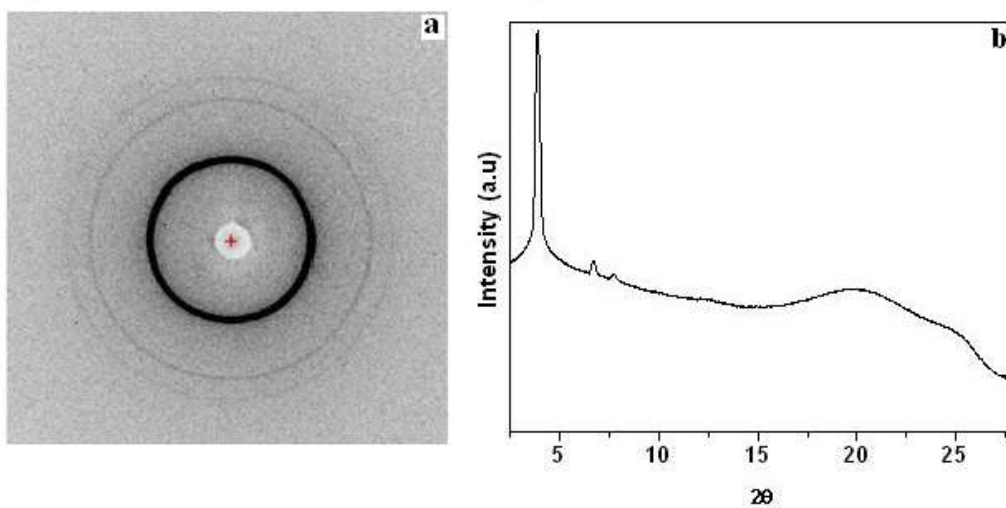
**Figure 6.** UV spectrum of the compound **18a**.



**Figure 7.** Optical Photomicrograph of compound **18a** obtained on cooling from the isotropic liquid at 35 °C (crossed polarizers, magnification X 200).

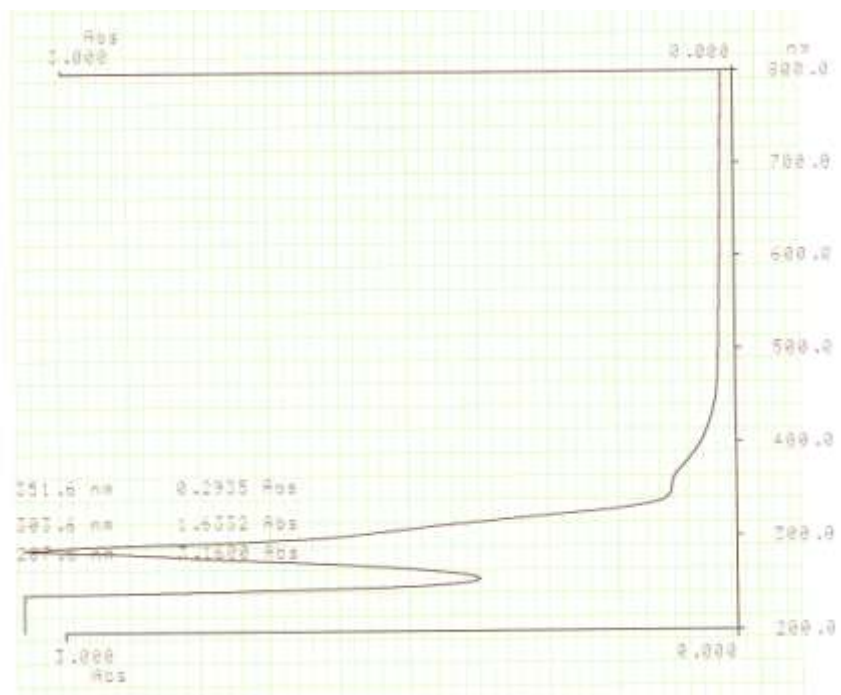


**Figure 8.** DSC traces of the compound **18a** on heating and cooling (scan rate  $2\text{ }^{\circ}\text{C min}^{-1}$ ).

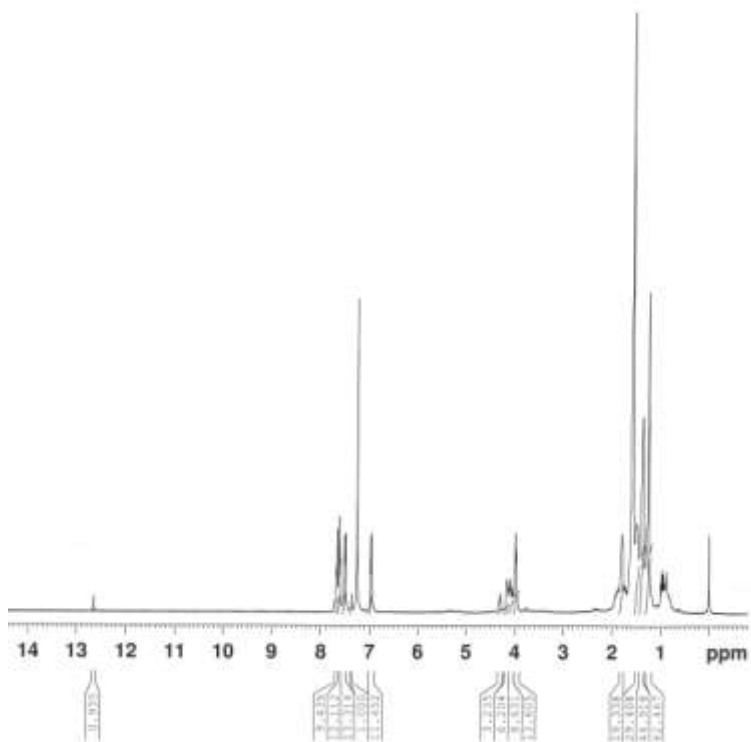


**Figure 9.** (a) X-ray diffraction pattern and (b) the one dimensional intensity versus  $2\theta$  (deg.) profile from X-ray diffraction for **18a** at room temperature ( $25\text{ }^{\circ}\text{C}$ ).





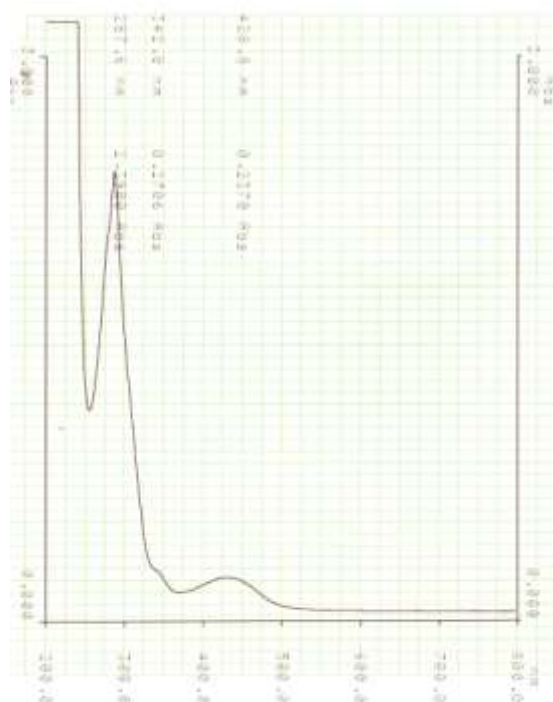
**Figure 12.** UV spectrum of the compound **19a**.



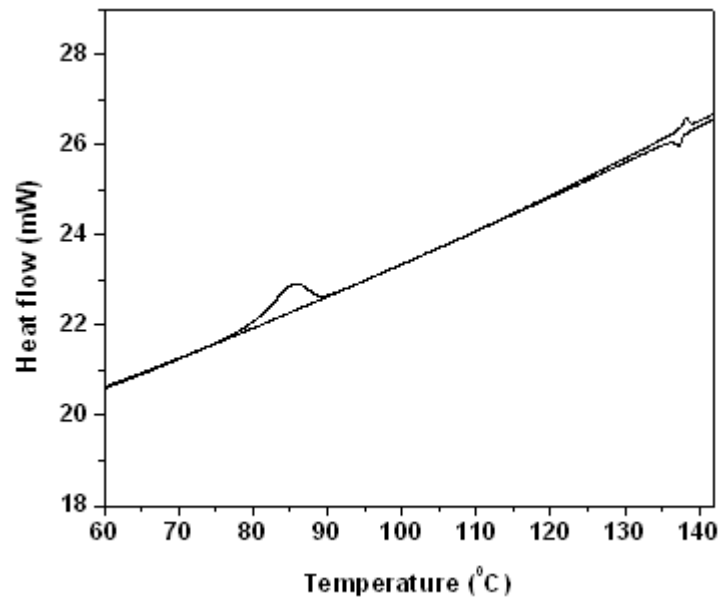
**Figure 13.**  $^1\text{H}$  NMR spectrum of the compound **20**.



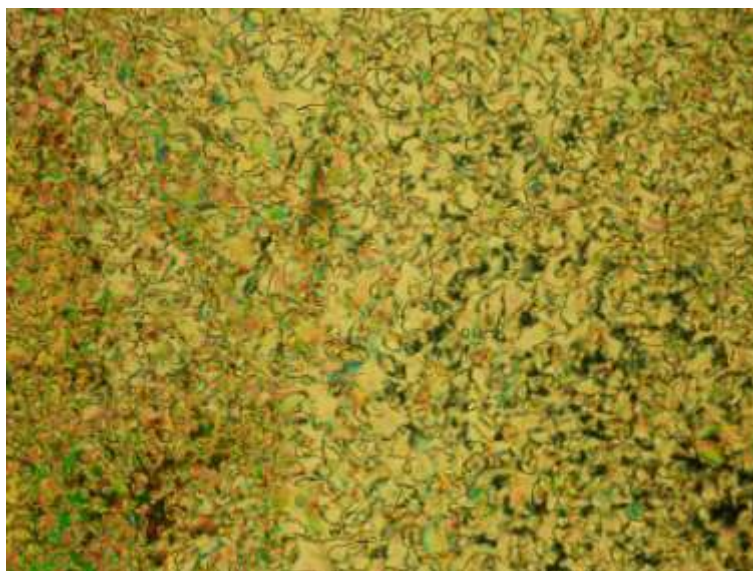
**Figure 14.** IR spectrum of the compound 20.



**Figure 15.** UV spectrum of the compound 20.

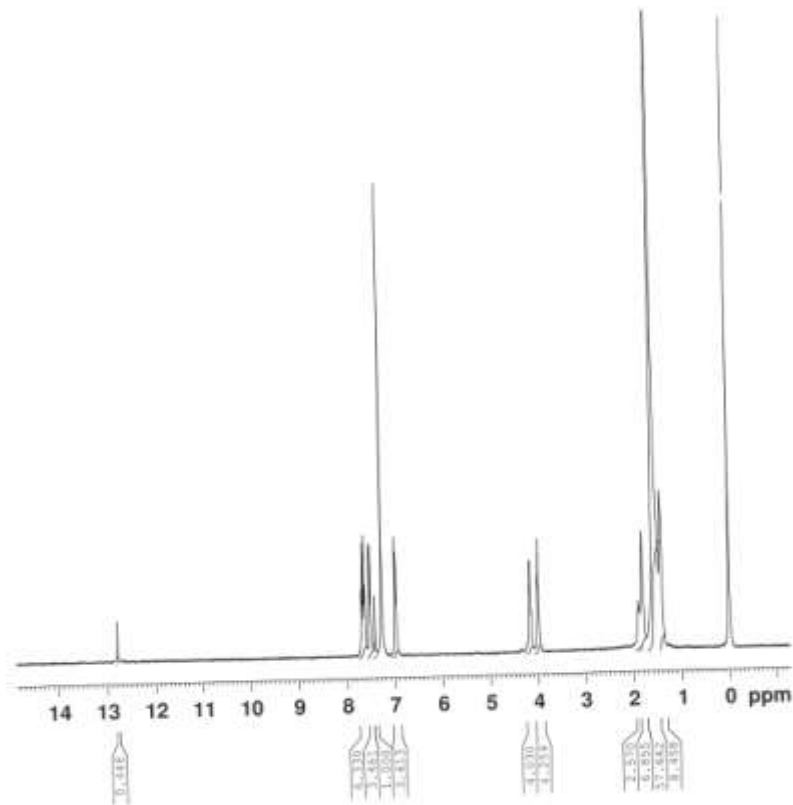


**Figure 16.** DSC traces for **20** on heating and cooling (scan rate  $5\text{ }^{\circ}\text{C min}^{-1}$ ).

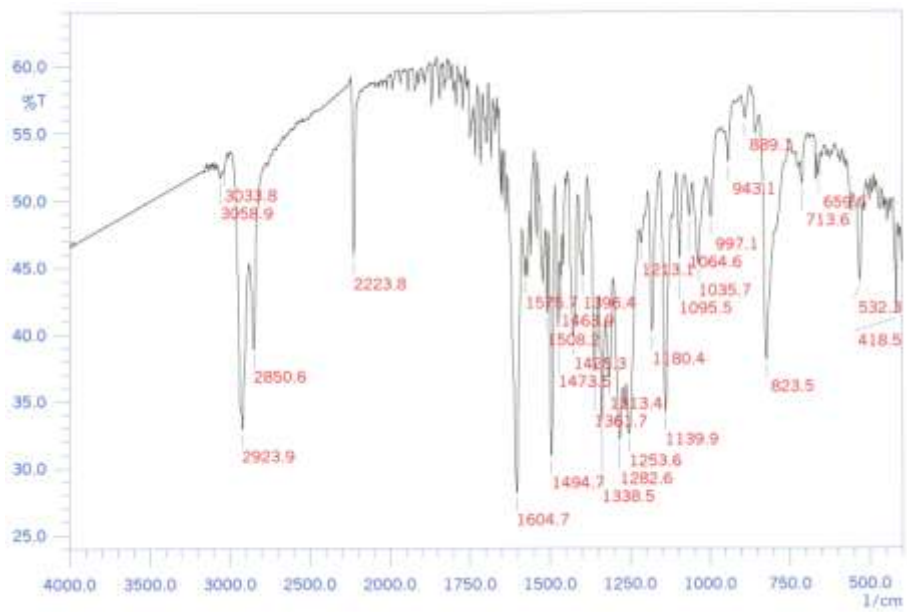


**Figure 17.** Optical texture of compound **20** obtained on cooling from the isotropic liquid at  $132\text{ }^{\circ}\text{C}$  (crossed polarizers, magnification, X 200).

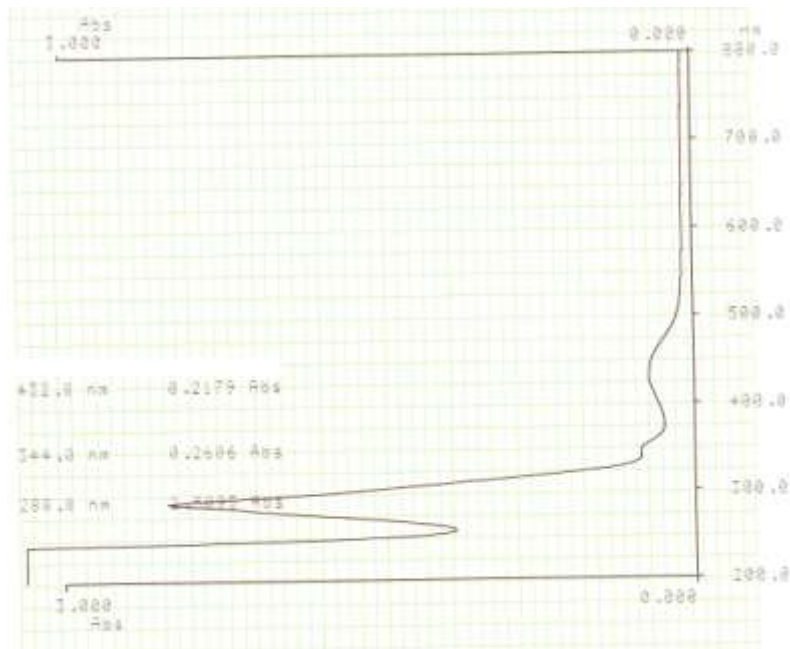




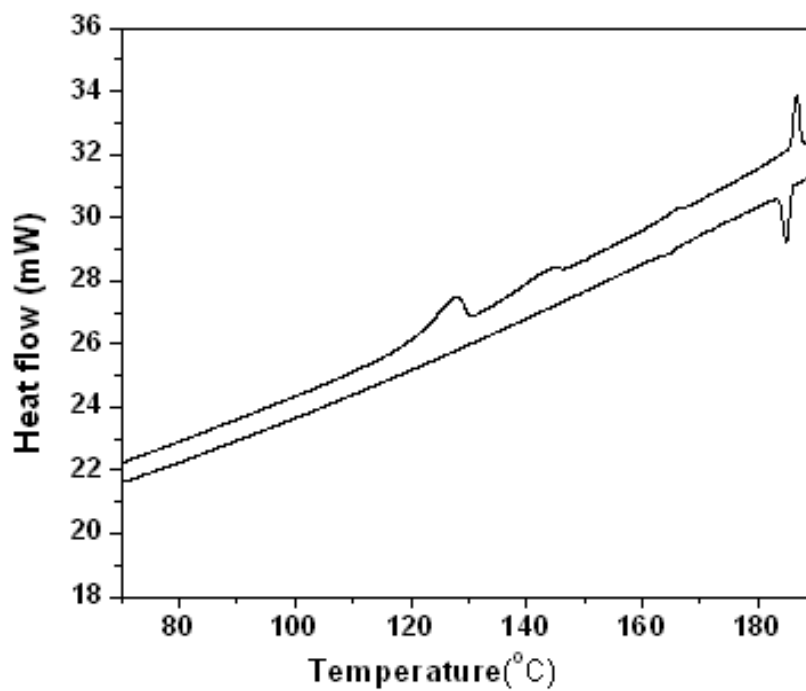
**Figure 18.**  $^1\text{H}$  NMR spectrum of the compound 23b.



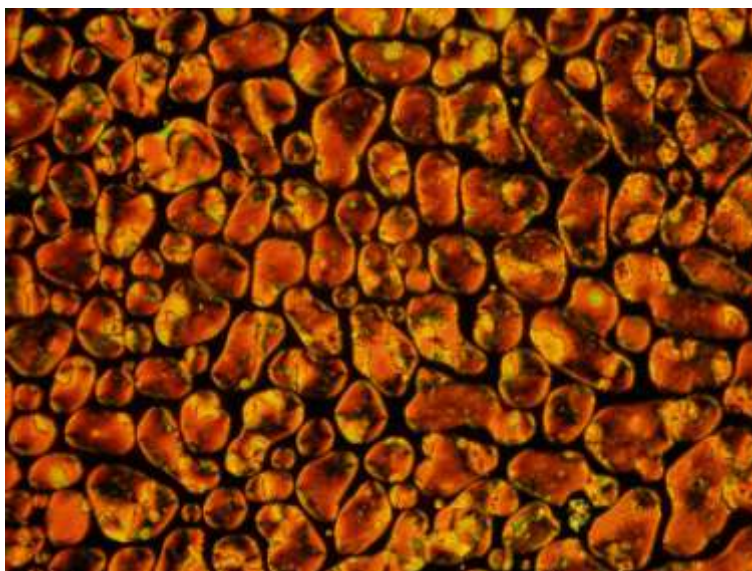
**Figure 19.** IR spectrum of the compound 23b.



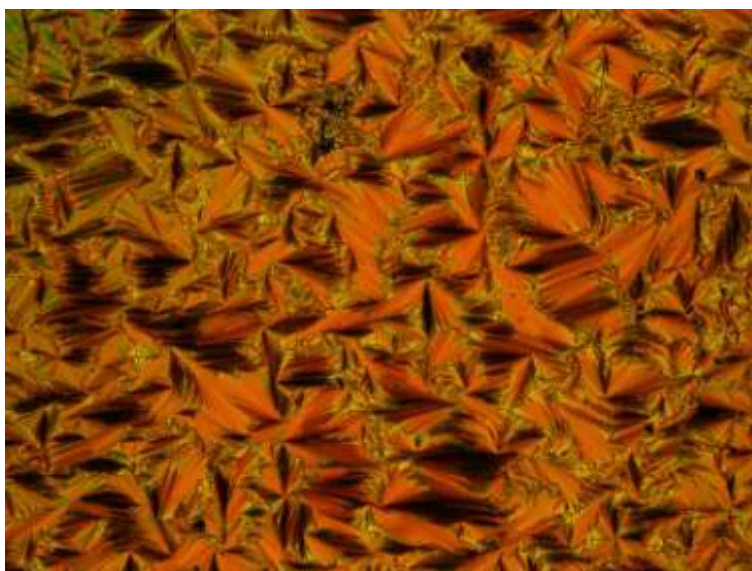
**Figure 20.** UV spectrum of the compound **23b**.



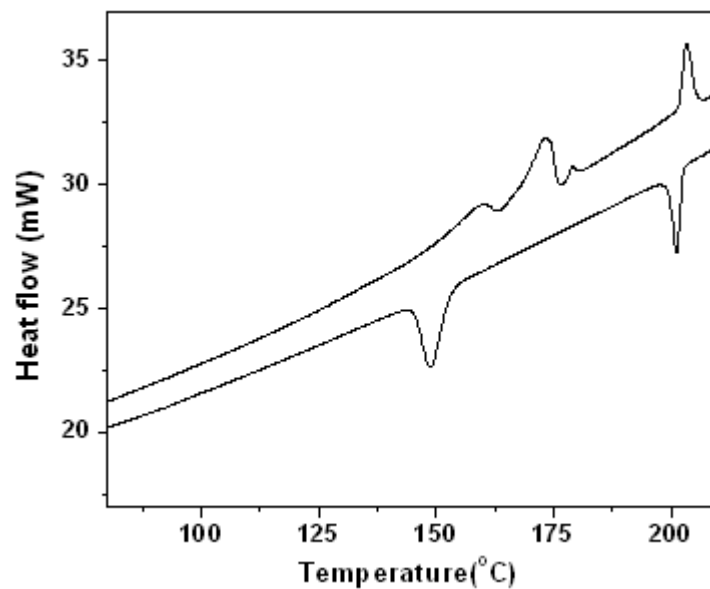
**Figure 21.** DSC traces of **23a** on heating and cooling (scan rate  $5\text{ }^{\circ}\text{C min}^{-1}$ ).



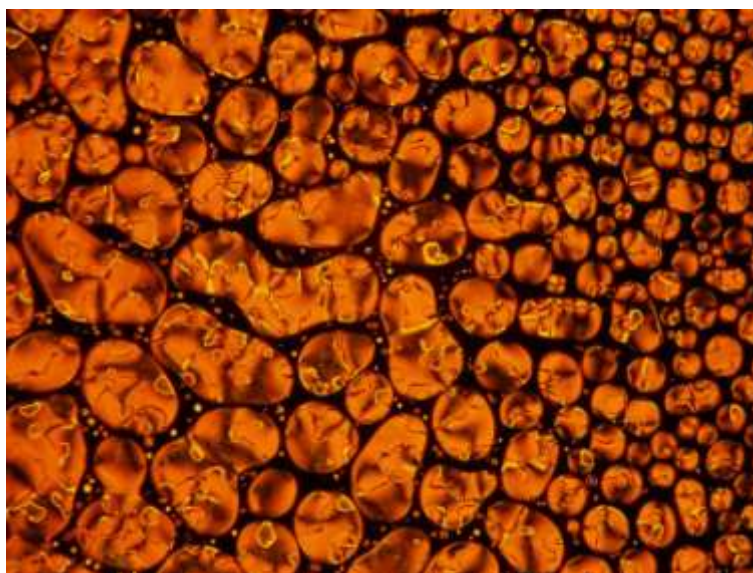
**Figure 22.** Optical texture of the N phase of compound **23a** obtained on cooling from the isotropic liquid at 180 °C (crossed polarizers, magnification X 200).



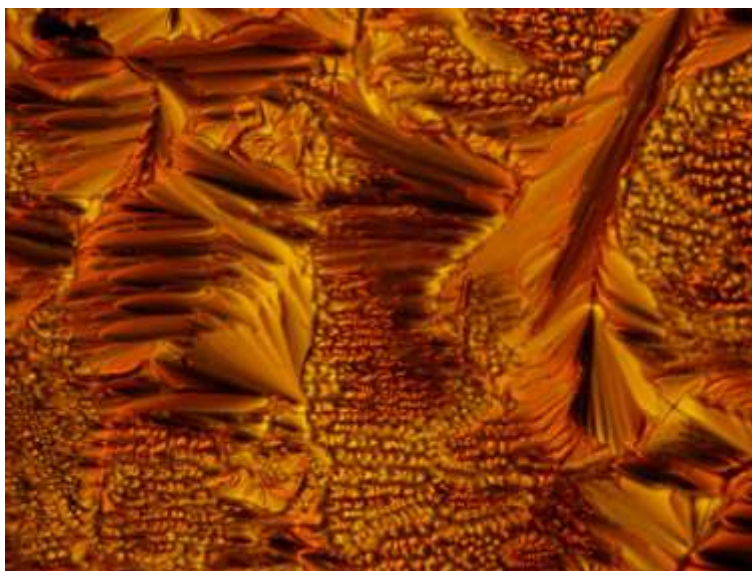
**Figure 23.** Optical texture of SmA phase of compound **23a** obtained on cooling from the isotropic liquid at 160 °C (crossed polarizers, magnification X 200).



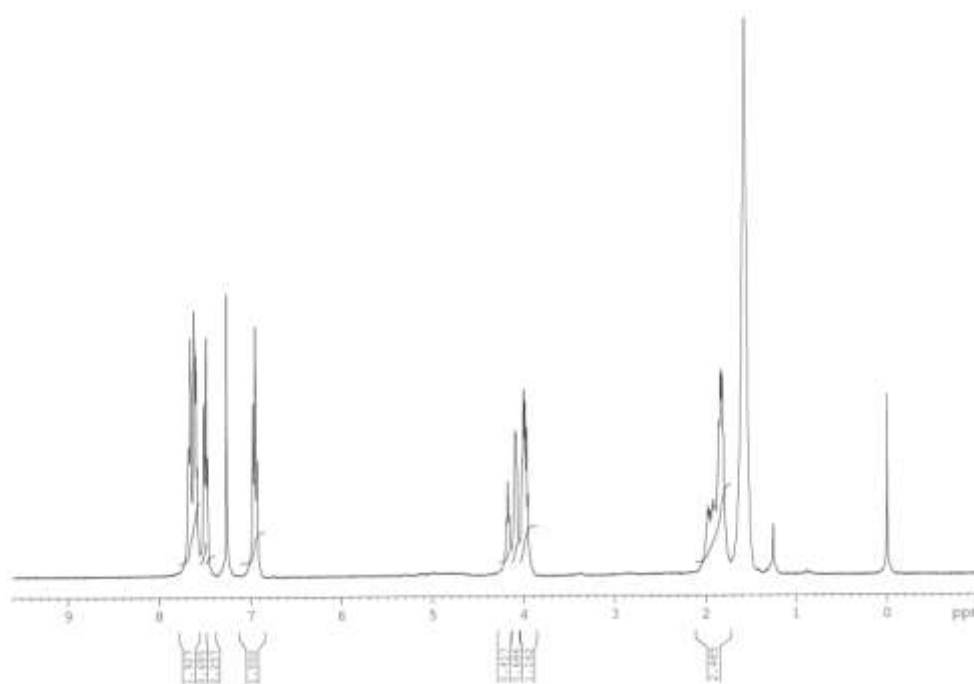
**Figure 24.** DSC traces for **23b** on heating and cooling ( $5\text{ }^{\circ}\text{C min}^{-1}$ ).



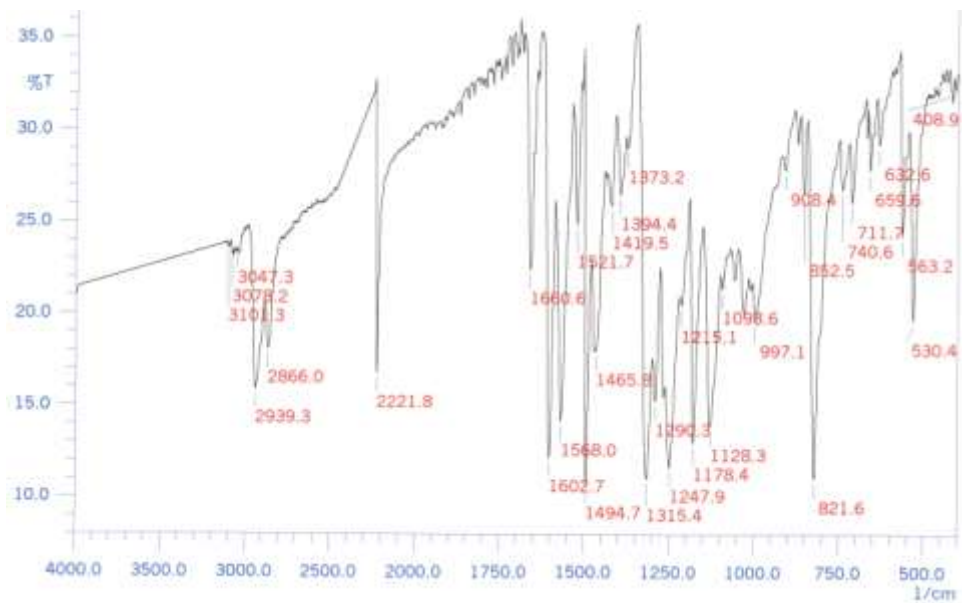
**Figure 25.** Optical texture of N phase of the compound **23b** obtained on cooling from the isotropic liquid at  $199\text{ }^{\circ}\text{C}$  (crossed polarizers, magnification X 200).



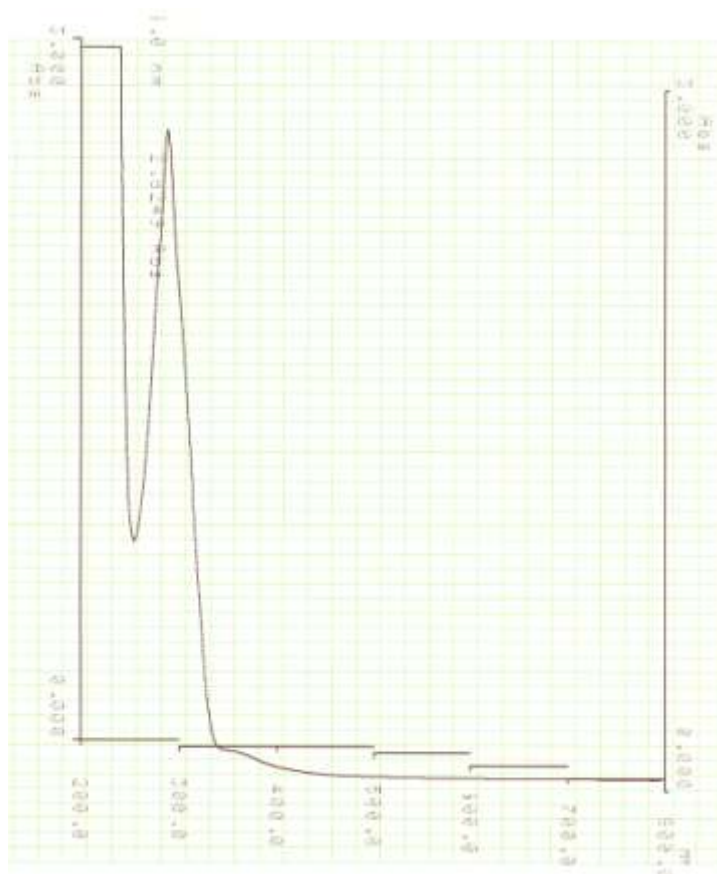
**Figure 26.** Optical texture of N phase of the compound **23b** obtained on cooling from the isotropic liquid at 160 °C (crossed polarizers, magnification X 200).



**Figure 27.** <sup>1</sup>H NMR spectrum of the compound **24a**.



**Figure 28.** IR spectrum of the compound **24a**.



**Figure 29.** UV spectrum of the compound **24a**.



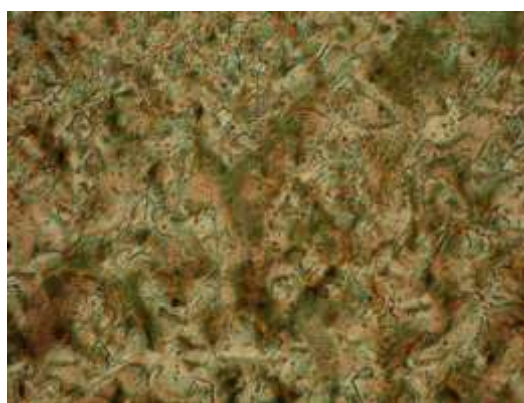
**Figure 30.** Optical texture of compound **24a** obtained on cooling from the isotropic liquid at 170 °C (crossed polarizers, magnification X 200).



(a)

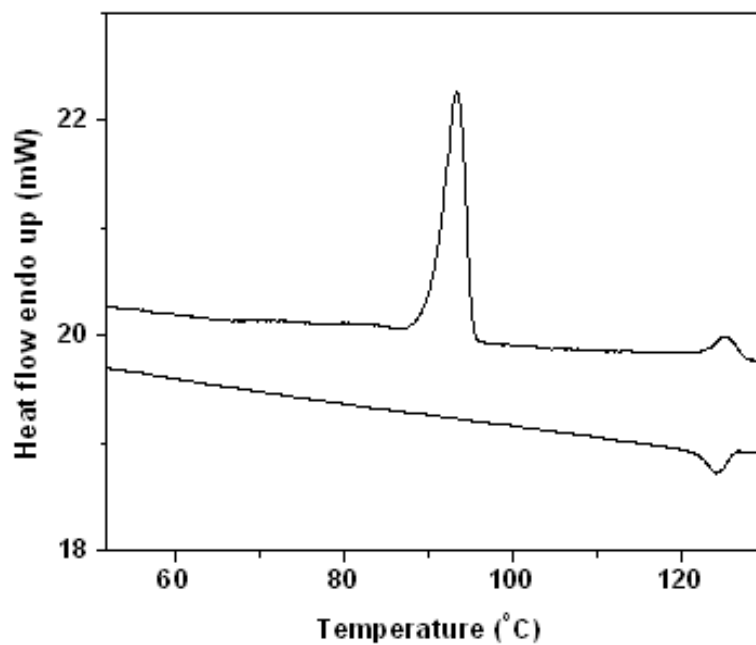


(b)



(c)

**Figure 31.** Optical texture of compound **24b** obtained on cooling from the isotropic liquid at (a) 120 & (b) 100 & (c) 70 °C respectively (crossed polarizers, magnification X 200).



**Figure 32.** DSC traces of compound **24c** on heating and cooling (scan rate 5 °C/ min)



**Figure 33.** Optical texture of compound **24c** obtained on cooling from the isotropic liquid at 120 °C (crossed polarizers, magnification X 200).