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Room-temperature discotic cholesteric and nematic phases: influence of 3,7-dimethyloctane peripheral chain on the molecular self-assembly of radial polyalkynylbenzene

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A series of novel radial symmetrical and non-symmetrical polyalkynylbenzene-based chiral and achiral disc-shaped materials with respectively five and six 3,7-dimethyloctyl peripheral aliphatic chains are synthesised. The symmetrical and non-symmetrical polyalkynylbenzene are prepared by Pd-catalysed alkynylation of hexaiodobenzene or monoalkoxypentabromobenzene with phenylacetylenes substituted by 3,7-dimethyloctyl peripheral chains. The molecular structures are confirmed by spectroscopic and spectrometric analysis. The phenylacetylene bearing 3,7-dimethyloctyl peripheral aliphatic chains via oxygen (OR) or directly to the phenyl ring (R) functions to balance steric and space-filling effects of the peripheral branched chains. Symmetrical molecules in which the peripheral aliphatic chain directly attaches to the R and OR functional groups exhibit the columnar and the nematic/cholesteric phases, respectively. By introducing non-symmetry to the disc shape, the mesophase is stabilised above and below room temperature. This molecular tailoring significantly affects the intermolecular attraction forces and as a result affects the melting, clearing temperatures and the molecular packing.

Keywords: discotic nematic liquid crystals; branching effect; Sonogashira coupling; columnar phase; polyalkynylbenzene

1. Introduction

Disc-shaped molecules can be used for a variety of optical and electronic applications [1–5]. The nematic phase (N_D) is rarely observed in disc-shaped molecules [6–9]. A negative birefringence film suitable for enlarging the viewing angle and enhancing the contrast ratio of commercial twisted nematic liquid crystal displays (TNLCDs), was the first commercial application of discotic nematic liquid crystals (DNLCs) [10, 11]. The discovery of the birefringence film for commercial application of N_D phases accelerated the synthesis of DNLCs [12–14]. The molecular shape is the most important factor that determines if and how the molecules are self-organised into liquid crystalline phases. A variety of molecular architectures have been designed and synthesised to exhibit the N_D mesophase over a wide thermal range. However, most of these molecules exhibit the N_D phase only above room temperature (RT) [15]. In 1987, Kohne and Praefcke reported discotic polyalkynylbenzene (PAB) molecules exhibiting the N_D phase [16, 17]. Since then, these PAB have become well known as disc-shaped molecules exhibiting the N_D phase. Further, PAB is an unsaturated discotic core, in which rotational freedom of the ethynyl groups prevents efficient stacking of the molecules and reduces the π–π interactions. These effects make it easier for PAB molecules to form the N_D phase.

In order to understand the structure–property relationships and to prepare RT N_D LCs, we chose PAB molecules primarily because a number of PAB compounds exhibit the N_D phase [18] and, therefore, some minor structural modifications may lead to materials having the N_D phases at RT. It is expected that increasing the size of the peripheral alkyl chains in PAB derivatives gradually decreases the melting and clearing temperatures [19, 20]. In PAB derivatives with peripheral aliphatic chains linked via a hetero atom such as oxygen, the melting and clearing temperatures are higher compared to when the aliphatic chains are directly attached to the ring [19, 20]. It is also known that if the peripheral aliphatic chains of various cores are branched, the mesophase is widened, but the type of the mesophase formed could also be affected by the introduction of branching in many cases [20]. We have called this effect the ‘branching effect’ for simplicity. Thus, we choose PAB core to study the influence of the 3,7-dimethyloctane branching tail and to study the symmetry effects on transition temperatures. For this purpose, a variety of chiral and achiral molecules were designed and synthesised to realise the N_D and discotic cholesteric liquid crystals at RT.

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2. Result and discussion

2.1 Samples and synthesis scheme

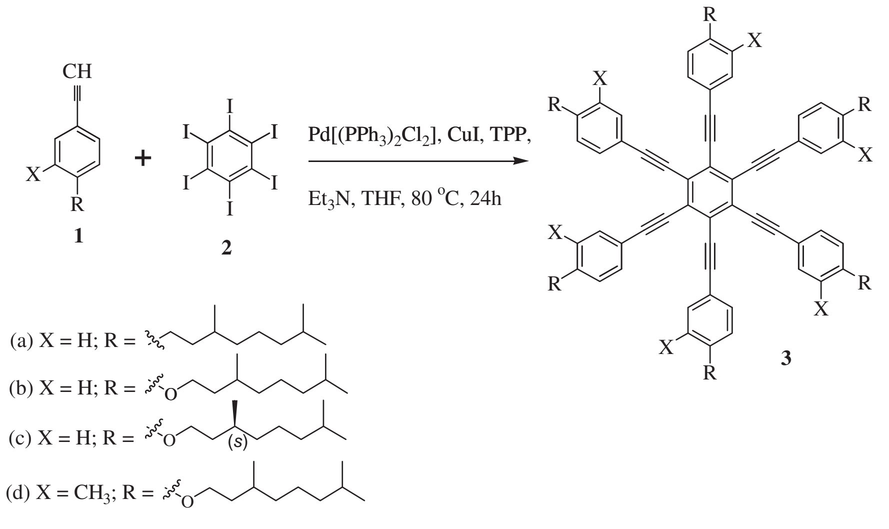
Two routes were employed to synthesise the terminal phenylacetylenes. The first route was dehydration reactions of phenylacetylene (compound **1a** in Scheme 1) and other phenyleneacetlyenes were prepared by Sonogashira coupling [21] as the second route. The syntheses of symmetrical and non-symmetrical PAB molecules are shown in Schemes 1 and 2. The adopted synthetic methods to prepare the 1-ethynyl-4-alknylbenzene (**1**) and 1-ethynyl-4-alkoxybenzene (**4**) are reported elsewhere [22]. Alkylation of *4*-iodophenol under classical reaction conditions gave 4-alkoxyiodobenzene. Further, 4-alkoxyiodobenzene was converted to phenylacetylenes (**6**) by a Sonogashira coupling reaction. The phenylacetylenes **1b** was prepared by alkylation of 4-iodophenol with (*S*)-3,7-dimethyloctylbromide, which was prepared by reduction of commercially available citernyl bromide (Aldrich #377716) with the Adams catalyst at RT (platinum (IV) oxide commonly known as the 'Adam's catalyst' was purchased from Sigma-Aldrich #206032 having 81–83% Pt composition). 4-Iodo-3-methylphenol was made by iodoination of 2-methylphenol (*O*-cresol) in the presence of iodoic acid. Further, the alkylation of 4-iodo-3-methylphenol under classical reaction conditions gave 3-methyl-4-alkoxyiodobenzene. It was converted to the required phenylacetylene **1** and **4** as discussed above.

A six- or five-fold Sonogashira reaction or Palladium coupling was used to attach the phenylacetylenes to a benzene central core. The reaction involves choices of the types of catalyst [$Pd(Ph_3P)Cl_2$], co-catalyst Cu^+ and solvents. A wide range of procedures are reported for such types of reaction [23]. Once the coupling reactions were carefully optimised, the reactions are straightforward. However, the purification of these materials was difficult, especially the removal of four/three-fold substituted isomers from the product, often reducing the yields of the reaction as discussed in the experimental section below. Alkyl- and alkoxy-substituted symmetrical PABs were prepared by a palladium-catalysed coupling of phenylacetylenes **1**, with hexaiodobenzene as shown in Scheme 1. Similarly, lateral methyl-substituted PABs were also prepared using the phenylacetylene (**6**) as shown in Scheme 2. The commercially available pentabromophenol (**4**) was alkylated to get monoalkoxy-pentabromobenzene **5** (Scheme 2) by a Mitsunobu reaction. Condensation of phenylacetylenes **6** with **5** yielded the desired PAB **7** by Sonogashira coupling.

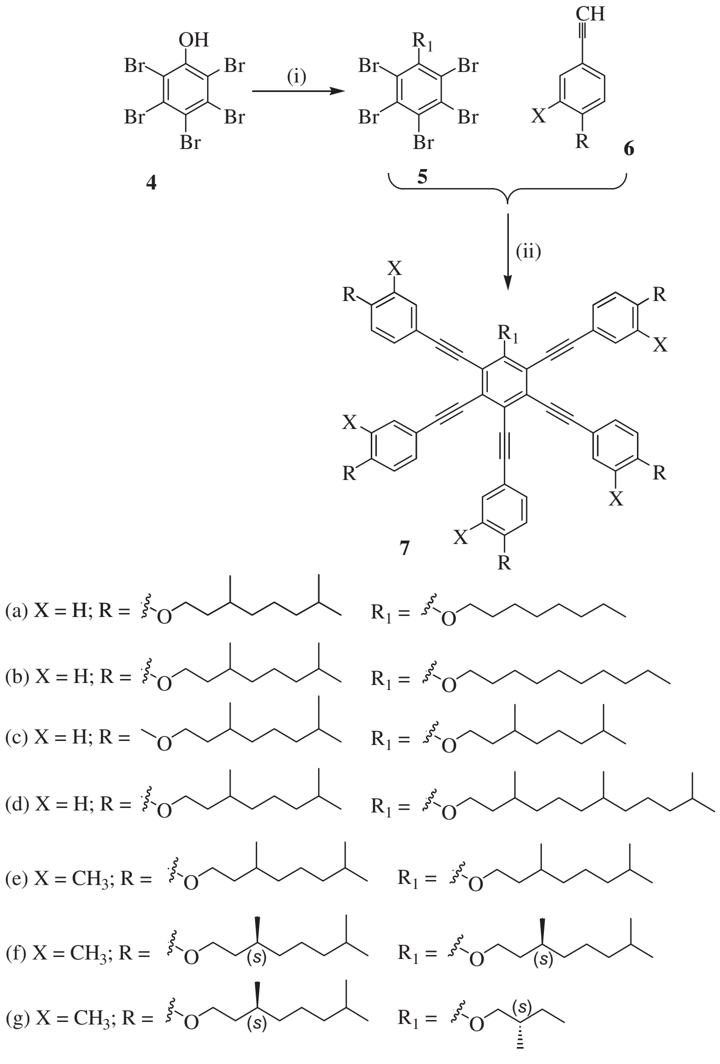
All the precursors and pre-precursors in our work were fully characterised by ^1H nuclear magnetic resonance (NMR), mass and infrared (IR) spectroscopy. All these compounds were liquid at RT. All the target compounds were confirmed by ^{13}C NMR and matrix-assisted laser desorption/ionisation-time-of-flight (MALDI-TOF)/fast atom bombardment (FAB) mass analysis also. Elemental analyses of all the compounds give correct values within the acceptable error range ±0.5%. All these data confirm that the compounds are highly pure. The spectral data of all the compounds are given in the experimental section.

2.2 Liquid crystalline properties

The textural microscope observations were carried out using polarising optical microscopy and the enthalpies associated with different transitions were determined using differential scanning calorimetry (DSC). In this study, we have synthesised four symmetrical and seven



Scheme 1. Synthesis of symmetrical PAB molecules.



Reagents and reaction conditions: (i) ROH, DIAD, PPh_3, THF, –10°C,15h.
(ii) $Pd[(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N, THF, 80 °C, 24h

Scheme 2. Synthesis of non-symmetrical PAB molecules.

non-symmetrical new PAB compounds. The transition temperatures and associated enthalpies obtained from DSC thermograms are given in Tables 1 and 2. All the compounds are thermally very stable as confirmed by the reproducibility of the thermograms on several heating and cooling cycles. The symmetrical PAB compound **3a** shows the columnar (Col) phase, whereas compounds **3b** and **3d** with a lateral substituted methyl show the N_D mesophase instead of the Col phase. Note on cooling that the N_D mesophase of compound **3d** crystallises at RT (27°C) and the thermal range of the mesophase is expanded. Compound **3c** shows the N_D* phase.

Table 1. Transition temperatures (°C) and transition enthalpies (kJ/mol^{-1}) of symmetrical PAB compound **3**.

Compound **3**	Heating scan	Cooling scan
(a)[a]	Col 78 I	I 76 Col
(b)	Cr 85.4 (57.2) N_D 132.5 (0.2) I	I 131.2 (0.1) N_D 68.5 (53.5) Cr
(c)	Cr 85.4 (56.4) N_D* 128.9 (0.2) I	I 124.7 (0.1) N_D* 66.0 (49.4) Cr
(d)[a]	Cr 73 N_D 158 I	I 157 N_D 27 Cr

Note: [a]Transition temperatures were observed by polarising optical microscopy.

All the non-symmetrical compounds **7** exhibit a nematic phase or viscous liquid at RT. Compounds **7a** and 7**c** are viscous liquids at RT irrespective of the existence of lateral methyl substitution. By increasing a chain length on the core, compound **7b** exhibits the N_D phase at RT. However, on further increasing the chain length on the core or introducing lateral methyl

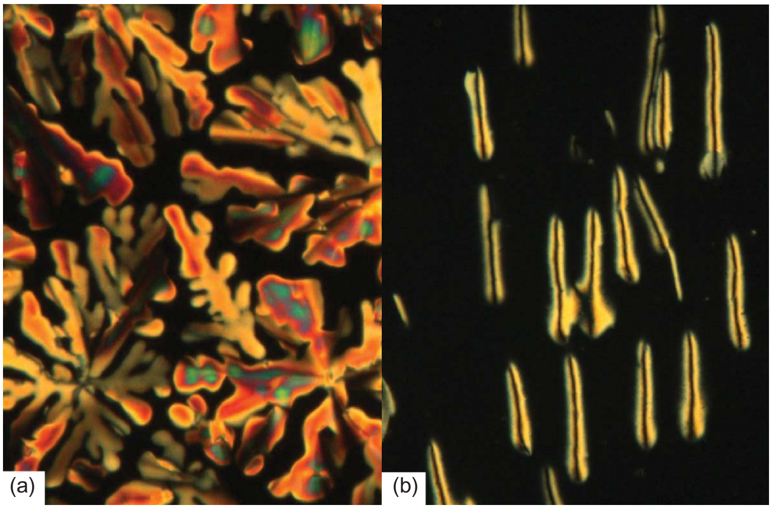


Figure 1. (a) Dendritic texture of the columnar mesophase of compound **3a** at RT. (b) The N_D mesophase of compound **7b** at RT.

Table 2. Transition temperatures (°C) and transition enthalpies (kJ/mol^{-1}) of non-symmetrical PAB compound **7**.

Compound **7**	Heating scan	Cooling scan
(a)	Viscous liquid at RT	
(b)	g -34.4 N_D 40.6 (0.2) I	I 39.8 (0.1) N_D -36.9 g
(c)	Viscous liquid at RT	
(d)	Viscous liquid at RT	
(e)	g -33.6 N_D 75.7 (0.09) I	I 75.2 (0.08) N_D -33.7 g
(f)	g -34 N_D* 88.5 (0.05) I	I 87.7 (0.05) N_D* -36 g
(g)[a]	N_D* 35.5 I	I 34.0 N_D*

Note: [a]Transition temperatures were observed by polarising optical microscopy.

substitution in R_1, compound **7d** loses the N_D phase but shows a highly viscous liquid at RT. Interestingly, introducing methyl substitutions ortho to the peripheral chains, compound **7e** exhibits the N_D and chiral compounds **7f** and **7g** exhibit the N_D* mesophase at RT. The N_D phase is stable well below and above the RT. The isotropisation temperature of the chiral compound **7f** is higher than that of the achiral compound **7e**. Thus we obtained compounds showing the N_D phase over a wide temperature range including RT by introducing asymmetry and methyl substitutions at ortho to peripheral chains.

Compound **3a,** on cooling from the isotropic liquid, forms a dendritic texture, as shown in Figure 1(a). From the texture, this phase appears to be the Col mesophase. However, we have not confirmed the Col phase by X-ray study at this moment. For compound **7b**, on cooling from the isotropic phase, birefringent textures first emerged and then disappeared to become a dark view after about 5 min. This view remained dark, indicating a homeotropic alignment. Sometimes, we observed a characteristic texture as shown in Figure 1(b). Further observations are necessary for identifying the molecular director map. It is worth mentioning that the tendency is much stronger in compound **7e**. Thus we can conclude that some of the present discotic molecules have a strong tendency to show a homeotropic alignment at a normal glass surface at RT, which could be of significant technological benefit in the future. The chiral compound **7f** shows an oily streak texture at RT, as shown in Figure 2. Several methods were trialled to obtain planar alignment to determine pitch without any success [24]. From the oily streaky texture we could estimate the cholesteric pitch to be approximately 2–3 μm.

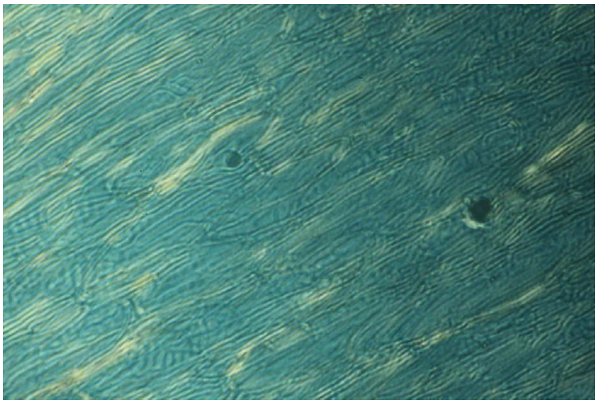


Figure 2. Oily strike texture of the discotic cholesteric phase of compound **7e** at RT.

3. Discussion

The thermal behaviour of compound **3a** obtained in different batches was sometimes not consistent although the spectral data are identical. Existence of diastereoisomers could be the cause of varying melting and clearing points in different batches. The clearing point was observed between 50°C and 80°C. Efforts to crystallise the material in various solvents at low temperature met with failure but fractionation of the product is possible by column chromatography over silica gel (240–400 mesh) and eluting with hexane-dichloromethane in small (~1 ml) fractions. The first few collections have relatively lower clearing points (50°C) than the latter fractions (70–80°C). This clearly indicates that compound **3a** with alkyl tails can be a statistical mixture of various diastereoisomers. Detailed work has been reported elsewhere [22].

PABs exhibit mesomorphism when the molecules have peripheral alkyl chains (branched or linear) with a chain length from C5 to C9 [22]. Molecular symmetry gives a remarkable effect on the transition temperatures of mesomorphism. All these symmetrical compounds with alkoxy tails exhibit the nematic or cholesteric mesophase above ambient temperature. The branching effect was not sufficient in these compounds. We broke the molecular symmetry and designed the compound **7** series, finding that the symmetrical compound **3b** and its chiral analogue **3c** respectively exhibit the N_D and N_D^* phases, whereas non-symmetrical compounds **7a, 7c** and **7d** are viscous liquids at RT. However, it is interesting to note that all of the compounds **7** exhibit the N_D mesophase below and above the ambient temperature, if we assume that a viscous liquid at RT exhibits the nematic phase below the ambient temperature. On replacing the racemic (3,7-dimethyloctane, mixture of *R* and *S*) branched chain (compounds **3b** and **7e**) with a chiral (*S*)-3,7-dimethyloctane (compounds **3c** and **7f**), racemic and chiral compounds exhibit the N_D and N_D^* mesophases, respectively, at different transition temperatures.

Chain length does have an effect, i.e. compound **7b** with a longer chain (R_1) exhibits the N_D phase at RT whereas compound **7a** with a short chain is liquid at RT. It was expected that the rotation of larger aliphatic chain lengths associated with a central benzene core would further reduce the intermolecular interactions which promote liquid crystallinity. Further, the introduction of the lateral methyl group could increase the clearing temperature of the compounds having identical branched chains. Indeed, compounds **7b** and **7e–g** so designed exhibit the N_D or N_D^* mesophase above and below the ambient temperature. Compounds **3b**, **3c**, **7e** and **7f** are good examples of the branching effect and the molecular symmetry effect on disc-shaped molecules. The effect of a methyl substituent supports the assumption of the existence of the N_D phase below viscous liquid, i.e. the hidden N_D or N_D^* phase below (viscous) isotropic liquid emerges at RT with the increase of the isotropisation temperature due to the introduction of a methyl substitution.

4. Experimental details

4.1 General

Commercially available chemicals and solvents were obtained and were used without further purification. All the reactions were carried out under an Argon atmosphere. The tetrahydrofuran (THF) was refluxed over sodium metal (Na) under argon atmosphere. Thin layer chromatography (TLC) was performed on a Merck, Kieselgel 60, F_{254}. ^{1}H and ^{13}C spectra were recorded on a Bruker 400 MHz spectrometer. The MALDI-TOF mass spectra were recorded on Kratos PC Axima CFR spectrometer and FAB mass spectra were recorded on a JEOL JMS 600H spectrometer with positive ion mode. Transition temperatures were determined by Perkin-Elmer DSC-Diamond series and DSC 7. Peak temperatures observed in the heating and cooling runs at the rate of 5°C min^{-1} were reported. Optical textures were observed using an Olympus BX51 polarising optical microscope equipped with a Mettler FP82HT hot stage.

4.2 General procedure for the preparation of symmetrical PAB compounds (3)

A mixture of phenylacetlyene **1** (50 mmol), C_6I_6 (5 mmol), PPh_3 (0.95 mmol) and $Pd[(PPh)_2Cl_2]$ (0.43 mmol) in dry Et_3N (15 ml) was deoxygenated and stirred under an argon atmosphere for 30 min. CuI (1 mmol) and dry THF (5 ml) were added to the reaction mixture under inert atmosphere and the mixture was stirred for 24 h at 80°C under an argon atmosphere. The mixture was allowed to cool at RT, and then filtered through Celite. The solvent was evaporated under vacuum and purified by repeated column chromatography over silica gel 240–400 mesh eluting petroleum ether with 0.5% of CH_2Cl_2.

3(a): 1,2,3,4,5,6-hexakis((4-(3,7-dimethyloctyl)phenyl) ethynyl)benzene. Yield 40%; yellow semisolid; IR (KBr): 2955, 2926, 2206, 1514, 1464, 1365, cm^{-1}; ^{1}H NMR: δ 7.55 (d, 12H, $J = 8$), 7.18 (d, 12H, $J = 8$), 2.63 (m, 12H), 1.66 (m, 12H), 1.55 (m, 12H), 1.03 (m, 12H), 1.13 (m, 24H), 0.94 (d, 18H, $J = 6.2$), 0.87 (d, 36H, $J = 6.6$); ^{13}C NMR: δ 144.3, 131.8, 128.5, 127.3, 120.6, 99.4, 87.1, 39.3, 38.7, 37.1, 33.6, 32.5, 29.7, 24.7, 22.6, 19.6; MS (FAB$^+$): 1522 [M + 2]$^+$. Elemental analysis: $C_{114}H_{150}$ (1520): calcd. C 90.06%, H 9.94%; found C 90.21%, H 9.81%.

3(b): 1,2,3,4,5,6-hexakis((4- (3,7-dimethyloctyloxy) phenyl)ethynyl)benzene. Yield 40%; yellow solid; IR (KBr): 2955, 2925, 2868, 2201, 1605, 1511, 1473, 1289, 1250, 1169, 1017 cm^{-1}; ^{1}H NMR: δ 7.55 (d, 12H, $J = 8.6$), 6.88 (d, 12H, $J = 8.6$), 4.03 (m, 12H), 1.85 (m, 6H), 1.58 (m, 24H), 1.29 (m, 24H), 1.17 (t, 6H, $J = 6.4$), 0.95 (d, 18H, $J = 6.5$), 0.87 (d, 36H, $J = 6.5$); ^{13}C NMR: δ 159.6, 133.2, 126.9, 115.3, 114.6, 99.0, 86.6, 66.4, 39.2, 37.2, 36.1, 29.8, 27.9, 24.6, 22.6, 19.6; MS (FAB^{+}): 1616 [M]$^{+}$. Elemental analysis: $C_{114}H_{150}O_6$ (1616): calcd. C 84.71%, H 9.35%; found C 84.31%, H 9.41%.

3(c): 1,2,3,4,5,6-hexakis((4-((*S*)-3,7-dimethyloctylo xy) phenyl)ethynyl)benzene. Yield 35%; bright yellow solid; IR (KBr): 2954, 2926, 2869, 2204, 1605, 1513, 1469, 1289, 1246, 1170, 1020 cm^{-1}; ^{1}H NMR: δ 7.55 (d, 12H, $J = 8.4$), 6.88 (d, 12H, $J = 8.4$), 4.03 (m, 12H), 1.84 (m, 6H), 1.57 (m, 18H), 1.33 (m, 18H), 1.17 (t, 18H, $J = 5$), 0.96 (d, 18H, $J = 6.4$), 0.87 (dd, 36H, $J = 6.4$); ^{13}C NMR: δ 159.6, 133.3, 126.9, 115.4, 114.6, 99.1, 86.6, 66.5, 39.3, 37.3, 36.2, 36.1, 32.8, 29.9, 29.7,27.0, 24.8, 24.3, 22.7, 22.6, 19.6; MS (MALDI-TOF): 1616 [M]$^{+}$. Elemental analysis: $C_{114}H_{150}O_6$ (1615): calcd. C 84.71, H 9.35; found C 84.41, H 9.55.

3(d): 1,2,3,4,5,6-hexakis((4-(3,7-dimethyloctyloxy)-3-methylphenyl)ethynyl)benzene. Yield 35%; yellow solid; IR (KBr): 2954, 2202, 1604, 1501, 1474, 1294, 1254, 1228, 1128 cm^{-1}; ^{1}H NMR: δ 7.47 (d, 12H, $J = 5$), 6.79 (d, 6H, $J = 8.9$), 4.04 (m, 12H), 2.19 (s, 18H), 1.87 (m, 6H), 1.61 (m, 18H), 1.31 (m, 18H), 1.17 (t, 18H, $J = 6.9$), 0.96 (d, 18H, $J = 6.5$), 0.87 (d, 36H, $J = 6.6$); ^{13}C NMR: δ 157.9, 134.2, 130.7, 127.0, 126.8, 114.9, 110.6, 99.3, 86.5, 66.3, 39.2, 37.2, 36.2, 29.9, 24.7, 22.6, 19.7, 16.1; MS (FAB^{+}): 1700 [M]$^{+}$. Elemental analysis: $C_{120}H_{162}O_6$ (1700): calcd. C 84.75%, H 9.60%; found C 84.41%, H 9.65%.

4.3 General procedure for preparation of pentabromoalkoxybenzene (4)

To a cooled (ice bath) solution of PPh$_3$ (100 mmol) in dry THF was added diisopropyl azodicarboxylate (Aldrich #22554-1, 100 mmol). The reaction mixture was stirred at RT for 10 min; alkyl alcohol (100 mmol) and pentabromophenol (100 mmol) were added. The ice bath was removed and the reaction mixture was stirred overnight at RT. The product was obtained by the usual workup in 40–80% overall yield. Finally, the product was purified by column chromatography (eluting Hexane-EtOAc 90:10). The analytical data of all these compounds were according to their chemical structure.

4.4 General procedure for the preparation of pentaalkynylbenzene (7)

This compound was prepared as mentioned previously for compound **3** but pentabromoalkoxybenzene (**4**) was used instead of C_6I_6 and it was purified by repeated flash column chromatography (hexane/dichloromethane 90:10).

7(a): 1,2,3,4,5-pentakis((4-(3,7-dimethyloctyloxy)phenyl)ethynyl)-6-(octyloxy)benzene. Yield 35%, yellow viscous liquid; IR (KBr): 2959, 2929, 2873, 2205, 1605, 1511, 1467, 1287, 1246, 1170, 1032 cm^{-1}; ^{1}H NMR: δ 7.52 (t, 10H, $J = 8.5$), 6.88 (m, 10H), 4.33 (t, 2H, $J = 6$), 4.02 (m, 10H), 1.84 (m, 10H), 1.59 (m, 10H), 1.26 (m, 44H), 0.95 (d, 18H, $J = 7.6$), 0.87 (d, 36H, $J = 6.5$); ^{13}C NMR: δ 159.9, 159.6, 159.5, 133.2, 133.1, 128.4, 123.8, 119.8, 115.6, 115.4, 114.6, 99.2, 99.1, 97.0, 86.6, 86.1, 83.5, 74.6, 66.4, 39.2, 37.3, 36.1, 31.9, 30.9, 29.8, 29.6, 29.3, 27.9, 26.3, 24.6, 22.6; MS (FAB^{+}): 1488 [M]$^{+}$. Elemental analysis: $C_{104}H_{142}O_6$ (1488): calcd. C 83.93%, H 9.62%; found C 83.61%, H 9.25%.

7(b): 1-(decyloxy)-2,3,4,5,6-pentakis((4-(3,7-dimethyloctyloxy)phenyl)ethynyl)benzene. Yield 35%; yellow viscous liquid; IR (KBr): 2959, 2929, 2873, 2205, 1605, 1511, 1467, 1287, 1246, 1170, 1032 cm^{-1}; ^{1}H NMR: δ 7.52 (t, 10H, $J = 8.5$), 6.88 (m, 10H), 4.33 (t, 2H, $J = 6$), 4.02 (m, 10H), 1.84 (m, 10H), 1.59 (m, 10H), 1.26 (m, 40H), 0.95 (d, 18H, $J = 7.6$), 0.87 (d, 30H, $J = 6.5$); ^{13}C NMR: δ 159.9, 159.6, 159.5, 133.2, 133.1, 128.4, 123.8, 119.8, 115.6, 115.4, 114.6, 99.2, 99.1, 97.0, 86.6, 86.1, 83.5, 74.6, 66.4, 39.2, 37.3, 36.1, 31.9, 30.9, 29.8, 29.6, 29.3, 27.9, 26.3, 24.6, 22.6; MS (FAB^{+}): 1516 [M]$^{+}$. Elemental analysis: $C_{106}H_{146}O_6$ (1516): calcd. C 83.96%, H 9.71%; found C 84.31%, H 10.25%.

7(c): 1-(3,7-dimethyloctyloxy)-2,3,4,5,6-pentakis(4-(3,7-dimethyloctyloxy)phenyl)ethynyl) benzene. Yield 35%; reddish yellow viscous liquid; IR (KBr): 2954, 2928, 2870, 2206, 1605, 1512, 1470, 1287, 1247, 1170 cm^{-1}; ^{1}H NMR: δ 7.53(m, 10H), 6.87 (m, 10H), 4.38 (m, 2H), 4.01 (m, 10H), 2.22 (m, 2H), 1.83 (m, 10H), 1.59 (m, 18H), 1.30 (m, 30H), 0.93 (d, 18H, $J = 6.4$), 0.85 (dd, 36H, $J = 6.5$); ^{13}C NMR: δ 159.9, 159.6, 159.5, 159.4, 133.2, 133.1, 128.4, 123.8, 119.8, 119.8, 115.6, 115.4, 114.6, 99.2 99.1, 97.0, 86.6, 86.1, 83.6, 72.9, 66.4, 39.2, 37.5, 37.2, 36.1, 29.8, 27.9, 24.6, 22.6 ; MS (FAB^{+}): 1514 [M]$^{+}$. Elemental analysis: $C_{106}H_{146}O_6$ (1516): calcd. C 83.96%, H 9.71%; found C 83.61%, H 9.65%.

7(d): 1,2,3,4,5-pentakis(((4-(3,7-dimethyloctyloxy)phenyl)ethynyl)-6-(3,7,11-trimethyldodecyloxy)benzene. Yield 35%; yellow very viscous liquid; IR (KBr): 2954, 2928, 2206, 1605, 1512, 1470, 1287, 1247, 1170 cm^{-1}; ^{1}H NMR: δ 7.53(m, 10H), 6.87 (m, 10H), 4.38 (m, 2H), 4.01 (m, 10H), 2.22 (m, 2H), 1.83 (m, 10H), 1.59 (m, 10H), 1.30 (m, 30H), 0.93 (d, 18H, $J = 6.4$), 0.85 (dd, 36H, $J = 6.5$); ^{13}C NMR: δ 159.9, 159.6, 159.5, 159.4, 133.2, 133.1, 128.4, 123.8, 119.8, 119.8, 115.6, 115.4, 114.6, 99.2 99.1, 97.0, 86.6, 86.1, 83.6, 72.9, 66.4, 39.2, 37.5, 37.2, 36.1, 29.8, 27.9, 24.6, 22.6 ; MS (FAB$^+$): 1516 [M]$^+$. Elemental analysis: $C_{111}H_{156}O_6$ (1586): calcd. C 84.04%, H 9.91%; found C 83.81%, H 9.65%.

7(e): 1-(3,7-dimethyloctyloxy)-2,3,4,5,6-pentakis((4--(3,7-dimethyloctyloxy)-3-methylphenyl)ethynyl)benzene. Yield 55%; yellow viscous liquid; IR (KBr): 2954, 2926, 2869, 2204, 1604, 1504, 1470, 1295, 1255, 1129, 1019 cm^{-1}; ^{1}H NMR: δ 7.24 (m, 10H), 6.78 (m, 5H), 4.35 (m, 2H), 4.02 (m, 10H), 2.19 (m, 15H), 1.85 (m, 10H), 1.35 (m, 50H), 0.96 (d, 18H, $J = 6.4$), 0.85 (dd, 36H, $J = 6.5$); ^{13}C NMR: δ 157.8, 134.2, 134.0, 130.7, 130.6, 128.5, 127.0, 123.9, 119.8, 114.9, 110.7, 99.5, 99.4, 97.2, 86.6, 86.1, 83.5, 72.9, 66.4, 39.2, 37.6, 37.3, 36.2, 30.0, 29.8, 28.0, 24.7, 22.7, 22.6, 19.7, 16.1.; MS (FAB$^+$): 1584 [M]$^+$. Elemental analysis: $C_{111}H_{156}O_6$ (1586): calcd. C 84.04%, H 9.91%; found C 84.24%, H 9.75%.

7(f): 1-(*S*)-(3,7-dimethyloctyloxy)-2,3,4,5,6-pentakis-((4-((*S*)-3,7-dimethyloctyloxy)-3-methylphenyl)ethynyl) benzene. Yield 38%; yellow very viscous liquid; IR (KBr): 2954, 2926, 2869, 2204, 1604, 1504, 1470, 1295, 1255, 1129, 1019 cm^{-1}; ^{1}H NMR: δ 7.45 (m, 10H), 6.88 (m, 5H), 4.37 (m, 2H), 4.03 (m, 10H), 2.20 (m, 15H), 1.85 (m, 10H), 1.58 (mm, 15H),1.33 (m, 35H), 0.96 (d, 18H, $J = 8$), 0.87 (dd, 30H, $J = 6.5$), 0.83 (dd, 6H, $J = 7$); ^{13}C NMR: δ 157.9, 157.8, 134.2, 134.0, 133.9, 130.7, 130.5, 128.4, 127.0, 119.7, 114.9, 110.6, 99.5, 99.3, 86.6, 83.4, 66.4, 39.3, 39.2, 37.2, 36.2, 29.9, 27.9, 24.7, 22.6, 19.7, 16.1.; MS (MALDI-TOF): 1585.6 [M]$^+$. Elemental analysis: $C_{111}H_{156}O_6$ (1586): calcd. C 84.04%, H 9.91%; found C 83.61%, H 10.21%.

7(g): 1, 2, 3, 4, 5 -pentakis((4 -((*S*) -3,7-dimethyloctyl oxy) -3 - methylphenyl)ethynyl)- 6-((*S*)-2-methylbuto xy)benzene. Yield 35%; yellow viscous liquid; IR (KBr): 2954, 2926, 2869, 2204, 1604, 1504, 1470, 1295, 1255, 1129, 1019 cm^{-1}; ^{1}H NMR: δ 7.40 (m, 10H), 6.79 (m, 5H), 4.25 (m, 1H), 4.15 (m, 1H), 4.02 (m, 10H), 2.19 (t, 18H, $J = 8$), 2.0 (m, 1H), 1.87 (m, 5H), 1.5 (m, 12H), 1.19 (m, 30H), 0.96 (d, 21H, $J = 6$), 0.87 (dd, 36H, $J = 6$); ^{13}C NMR: δ 157.8, 157.7, 157.6, 134.2, 134.0, 133.9, 130.7, 130.5, 130.4, 128.5, 126.9 123.7, 119.6, 115.1, 114.9, 114.8, 110.6, 99.5, 99.3, 86.5, 83.5, 66.3, 39.2, 37.2, 36.1, 36.0, 29.9, 27.9, 26.4, 22.6, 19.7, 16.8, 16.1, 16.0 ; MS (MALDI-TOF): 1515.6 [M]$^+$. Elemental analysis: $C_{106}H_{146}O_6$ (1516): calcd. C 83.96%, H 9.71%; found C 83.81%, H 9.95%.

5. Conclusions

A series of symmetrical and non-symmetrical PAB compounds were synthesised. These molecules exhibit the nematic or chiral nematic phase in wide temperature ranges. The influence of the 3,7-dimethyloctane peripheral chain on PAB molecules and the structural–property relationship of these molecules has been discussed. The alkynyl-substituted compounds (R) have the stereoheterogeneity problem that affects the transition temperatures. To overcome this problem, alkoxy-substituted compounds were prepared. These compounds are thermally well stable. The effects of molecular symmetry and methyl substitution were examined. We found that most of the symmetrical and non-symmetrical molecules exhibit the N_D mesophase in a wide thermal range. In particular, the non-symmetrical ones exhibit the nematic or cholesteric mesophases well below and above the ambient temperature. The introduction of a methyl substituent increases the isotropisation temperature in both symmetrical and non-symmetrical compounds. As a result, in non-centrosymmetric compounds, viscous liquid at RT changes to the N_D or N_D^* phase at RT in methyl substituted compounds. This fact in turn suggests there exists a N_D or N_D^* phase below viscous liquid even in compounds without a methyl substitution.

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