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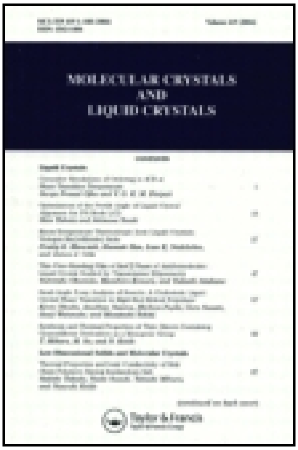

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New Mixed Tail Triphenylene Discotic Liquid Crystals

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Some new mixed tail triphenylene discotic liquid crystals having three alkoxy and three alkanoyloxy chains have been prepared and characterized. Effects of unsymmetrical substitution by virtue of different alkyl chains in the periphery and their attachment to the core were studied. The synthesis was carried out by esterification of the symmetrical and unsymmetrical trihydroxy-tripentyloxytriphenylenes with various acid chlorides. All the mixed tail triphenylene derivatives stabilize the mesophase range compared to the hexaether or hexaester derivatives of triphenylene. Nonsymmetric isomers have a broader mesophase range than the symmetric isomers.

Keywords: Discotic liquid crystals; triphenylene; mixed tail triphenylenes; columnar mesophase

INTRODUCTION

The nature of aliphatic side chains plays important role in deciding the thermal behavior and mesophase structures formed by disc-shaped molecules. The first generation of discotic liquid crystals were the symmetrically substituted hexaethers, thioethers, esters or benzoates of various flat or nearly flat, rigid aromatic cores such as benzene, triphenylene, truxene, *etc.* [1]. Triphenylene derivatives are the most widely synthesized and extensively studied discotic liquid crystals. The potential uses of these materials as one-dimensional conductors [2], photoconductors [3] and light emitting diodes [4] are attracting considerable attention. Several

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research groups are currently working on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene discotic liquid crystals [5].

Symmetrically substituted hexaethers of triphenylene are known to form an ordered hexagonal columnar (D_{ho}) mesophase [6] with the exception of hexabutyloxytriphenylene which was very recently reported to be more ordered than the D_{ho} phase and referred to a plastic discotic D_p phase [3e]. When the linking atom is sulfur instead of oxygen, these hexaalkylthiotriphenylenes commonly form hexagonal disordered (D_{hd}) phases [7]. One member of this series, hexahexylthiotriphenylene was proved to form a highly ordered helical phase in addition to the D_{hd} phase [8]. When the aliphatic chains are attached *via* an ester linkage such triphenylene hexaesters and benzoates show rich polymorphism and the formation of a tilted columnar phase D_t, a rectangular disordered columnar phase D_{rd} and a nematic discotic N_D phase, has been reported [6]. When the peripheral phenyl groups of these benzoates were laterally substituted with alkyl groups, transition temperatures changed significantly [9]. Stabilization of the columnar phase was achieved by inserting oxygen atoms in the side chain, the so called β-oxygen effect [10], or by using fluoroalkylated chains [11]. When one out of the six ether side chains in hexaalkoxytriphenylenes was replaced by an ester group, the stability of the mesophase enhanced significantly [12]. Mesophase stabilization due to steric hindrance of ester group has been discussed by Spiess and co-workers [12]. A plastic columnar discotic phase is also reported in this type of unsymmetric triphenylene derivatives [13].

To understand the origin of different mesophases in discotic liquid crystals at the molecular level, we have recently initiated a research program focusing on the synthesis of various triphenylene derivatives. We have very recently reported a highly improved synthesis of symmetrical, unsymmetrical and mono-functionalized triphenylene derivatives using a novel reagent $MoCl_5$ [5]. We have also reported earlier the synthesis of various functionalized triphenylenes [14], mixed tail triphenylene [15], low symmetry, fluorescent triphenylene [16] and core functionalized triphenylene discotic LCs [17].

Recently, we have found a simple and high yielding process for the preparation of symmetrical and unsymmetrical trialkoxy-trihydroxytriphenylenes [18]. As the steric bulk, out of the molecular plane, dipolar interaction of ester groups and length of alkyl chains could be responsible for different mesophase formation in triphenylene hexaesters and benzoates, we esterified the three hydroxy groups of the symmetrical and unsymmetrical trihydroxy-tripentyloxytriphenylenes with various acid chlorides. Here

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we report on the synthesis, characterization and mesomorphic properties of twelve such new mixed tail triphenylene derivatives.

EXPERIMENTAL

General Information

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. Column chromatographic separations were performed on silica gel (70–230 and 200–400 mesh). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer. All chemical shifts are reported in δ (ppm) units downfield from Me_4Si, and J values are given in Hz. All the acid chlorides were prepared from corresponding acids using thionyl chloride or oxalyl chloride. Symmetrical and unsymmetrical trihydroxy-tripentyloxytriphenylenes were prepared as reported by us recently [18]. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMFRT polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin–Elmer). The heating and cooling rate was 10°C/min. Synthesis of different triphenylene derivatives is outlined in Scheme 1.

Synthesis of Mixed Tail Triphenylene Derivatives

Typical procedure: To a magnetically stirred solution of 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene **1** (0.1 mmol) or 2,7,10-trihydroxy-3,6,11-tripentyloxytriphenylene **2** (0.1 mmol) and 4-dimethylaminopyridine (10 mmol%) in dry pyridine (2 ml, deoxygenated) was added different acid chloride (0.6 mmol) at 0°C under argon. The resultant suspension was stirred for 48 hrs. The reaction mixture was poured into ice-cold aqueous 0.01N HCl (5 ml) and extracted with ether (3 × 10 ml). The combined ether extracts were washed with water, brine and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the resultant crude product was purified by column chromatography over silica gel. Elution with hexane-ethyl acetate afforded a white solid that was recrystallized with absolute alcohol. Yields 60–70%.

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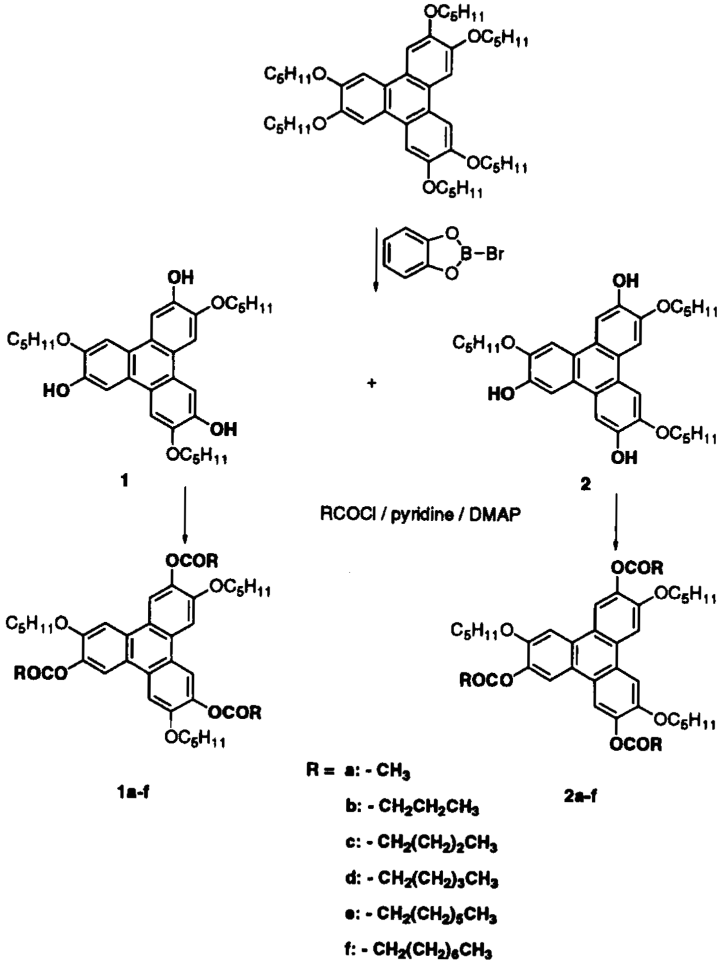

SCHEME 1 Synthesis of mixed tail triphenylene derivatives.

^{1}**H NMR data**: **1a**: 7.90 (s, 3H), 7.55 (s, 3H), 4.12 (*t*, $J = 6.6$, 6H), 2.41 (s, 9H), 1.85 (m, 6H), 1.46 (m, 12H) and 0.98 (*t*, $J = 7.0$, 9H)

1b: 7.87 (s, 3H), 7.51 (s, 3H), 4.09 (*t*, $J = 6.6$, 6H), 2.65 (*t*, $J = 7.3$, 6H), 1.90 (m, 12H), 1.46 (m, 12H), 1.16 (*t*, $J = 7.4$, 9H) and 0.97 (*t*, $J = 6.8$, 9H)

1c: 7.87 (s, 3H), 7.49 (s, 3H), 4.09 (*t*, $J = 6.6$, 6H), 2.67 (*t*, $J = 7.2$, 6H), 1.90 (m, 12H), 1.55 (m, 18H), 1.04 (*t*, $J = 7.2$, 9H) and 0.97 (*t*, $J = 6.8$, 9H).

1d: 7.88 (s, 3H), 7.52 (s, 3H), 4.10 (*t*, $J = 6.7$, 6H), 2.66 (*t*, $J = 7.3$, 6H), 1.86 (m, 12H), 1.50 (m, 24H) and 0.97 (m, 18H)

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1e: 7.85 (s, 3H), 7.43 (s, 3H), 4.07 (*t*, $J = 6.7$, 6H), 2.67 (*t*, $J = 7.2$, 6H), 1.87 (m, 12H), 1.52–1.2 (m, 36H) and 0.97 (m, 18H)

1f: 7.82 (s, 3H), 7.47 (s, 3H), 4.09 (*t*, $J = 6.7$, 6H), 2.67 (*t*, $J = 7.5$, 6H), 1.87 (m, 12H), 1.5–1.2 (m, 42H), 0.92 (*t*, $J = 7.0$, 9H) and 0.87 (*t*, $J = 6.7$, 9H)

2a: 8.06 (s, 1H), 7.96 (s, 1H), 7.93 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.74 (s, 1H), 4.20 (m, 6H), 2.42 (s, 3H),), 2.39 (s, 3H), 2.38 (s, 3H), 1.89 (m, 6H), 1.46 (m, 12H) and 0.97 (m, 9H)

2b: 8.04 (s, 1H), 7.92 (s, 1H), 7.91 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 4.19 (m, 6H), 2.65 (m, 6H), 1.88 (m, 12H), 1.38 (m, 12H), 1.13 (m, 9H) and 0.97 (m, 9H)

2c: 8.04 (s, 1H), 7.92 (s, 1H), 7.89 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 4.19 (m, 6H), 2.65 (m, 6H), 1.83 (m, 12H), 1.52 (m, 18H) and 0.99 (m, 18H)

2d: 8.08 (s, 1H), 7.99 (s, 1H), 7.97 (s, 1H), 7.85 (2s, 2H), 7.77 (s, 1H), 4.20 (m, 6H), 2.65 (m, 6H), 1.86 (m, 12H), 1.45 (m, 24H) and 0.97 (m, 18H)

2e: 8.05 (s, 1H), 7.94 (s, 1H), 7.91 (s, 1H), 7.82 (s, 1H), 7.80 (s, 1H), 7.73 (s, 1H), 4.19 (m, 6H), 2.64 (m, 6H), 1.83 (m, 12H), 1.52 (m, 36H) and 0.92 (m, 18H)

2f: 8.01 (s, 1H), 7.86 (s, 1H), 7.84 (s, 1H), 7.78 (s, 1H), 7.76 (s, 1H), 7.68 (s, 1H), 4.18 (m, 6H), 2.64 (m, 6H), 1.85 (m, 12H), 1.5 (m, 42H) and 0.97 (m, 18H)

^{13}C NMR data: **1c**: 172.07, 149.33, 139.11, 128.21, 121.96, 117.68, 105.75, 68.23, 33.94, 29.22, 28.24, 27.42, 22.67, 22.41, 14.09 and 13.84

2c: 171.87, 171.75, 171.68, 149.87, 149.57, 149.47, 140.43, 140.22, 139.85, 128.19, 127.33, 127.10, 123.54, 123.35, 122.38, 117.36, 116.76, 116.56, 113.73, 106.42, 105.82, 68.69, 33.88, 29.10, 28.32, 27.20, 22.56, 22.37, 14.05 and 13.78

RESULTS AND DISCUSSION

The key precursors for the preparation of triphenylene derivatives having three ether and three ester chains are the symmetrical (**1**) and nonsymmetrical (**2**) trifunctionalized triphenylenes. Having an easy access to these derivatives by our new method [18] allowed us to prepare two new mixed tail triphenylene series. In these derivatives we kept the ether chains (pentyloxy) constant and varied the number of carbons in the ester chains. Thus, classical esterification of 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene **1** and 2,7,10-trihydroxy-3,6,11-tripentyloxytriphenylene **2** with various acid

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chlorides give the 2,6,10-trialkanoyloxy-3,7,11-tripentyloxytriphenylene **1a–f** (series 1) and 2,7,10-trialkanoyloxy-3,6,11-tripentyloxytriphenylene **2a–f** (series 2). All the new compounds were characterized from their spectral analysis. The ^{1}H NMR of the symmetrical mixed tail triphenylene derivatives show, as expected, only two singlets for six (three each) aromatic protons but, interestingly, all the six aromatic protons of nonsymmetrical derivatives appear as six distinct singlets in addition to the expected signals for all other aliphatic protons. Similarly, the ^{13}C NMR of symmetrical derivative **1c** show only six peaks (each for three aromatic carbons), one peak for three carbonyl carbons and nine other peaks for twenty seven aliphatic carbons while all the eighteen aromatic carbons are resolved in the ^{13}C NMR of nonsymmetrical derivative **2c**.

The thermal data of all the new compounds (**1a–f** and **2a–f**) are collected in Table I, Figures 1 and 2. The lowest homologue of the series 2 *i.e.*, **2a** is nonmesomorphic and shows crystal to isotropic transition at 146.5°C. On cooling it crystallizes at 124°C. In contrary to this, the lowest homologue of the series 1 *i.e.*, **1a** shows crystal to isotropic transition at 185°C on heating but on cooling it comes to a highly ordered mesophase. Its texture resembles very well with that of highly ordered discotic plastic phase of hexabutyloxytriphenylene [3e]. This monotropic mesophase has a high crystallization tendency and starts to crystallize in the mesophase. The highest homologue of the series 1 (**1f**) is again non liquid crystalline. It is in fact a viscous oil at room temperature and crystallizes only upon cooling below 0°C. On heating it shows the isotropic peak at 31.5°C in the DSC and

TABLE I Phase transition temperatures and enthalpies of new mixed tails triphenylene derivatives. Cr = crystal, Col$_h$ = hexagonal columnar mesophase, I = isotropic. Temperatures are given in °C and the numbers in parenthesis indicate the enthalpy of the transition (ΔH) in kJ/mol

Compound	*Thermal behaviour*	
	Ist heating	*Ist cooling*
1a	Cr 185.0 (48.9) I	I 165.1 (3.7) M [a] 148.0 (44.2) CR
1b	Cr 132.7 (7.8) Col$_h$ 253.9 (13.1) I	I 249.1 (11.7) Col$_h$
1c	Cr 130.6 (17.1) Col$_h$ 244.6 (20.8) I	I 241.4 (19.8) Col$_h$
1d	Cr 109.9 (15.7) Col$_h$ 218.4 (14.7) I	I 214.5 (12.8) Col$_h$
1e	Cr 61.8 (14.6) Col$_h$ 168.3 (3.1) I	I 164.0 (3.8) Col$_h$
1f	Cr 31.5 (16.4) I	I7-(−25) Cr
2a	Cr 146.5 (27.2) I	I 124.1 (23.6) Cr
2b	Cr 61.7 (17.9) Col$_h$ 230.2 (14.9) I	I 225.5 (13.9) Col$_h$
2c	Cr 82.5 (26.3) Col$_h$ 227.6 (15.9) I	I 225.0 (16.3) Col$_h$
2d	Cr 69.2 (16.6) Col$_h$ 203.3 (6.5) I	I 200.5 (6.8) Col$_h$
2e	Cr 61.9 (22.6) Col$_h$ 155.3 (0.2) I	I 149.5 (0.3) Col$_h$
2f	Cr 56.5 (24.1) Col$_h$ 126.7 (1.7) I	I 120.8 (0.2) Col$_h$

[a] Monotropic metastable phase.

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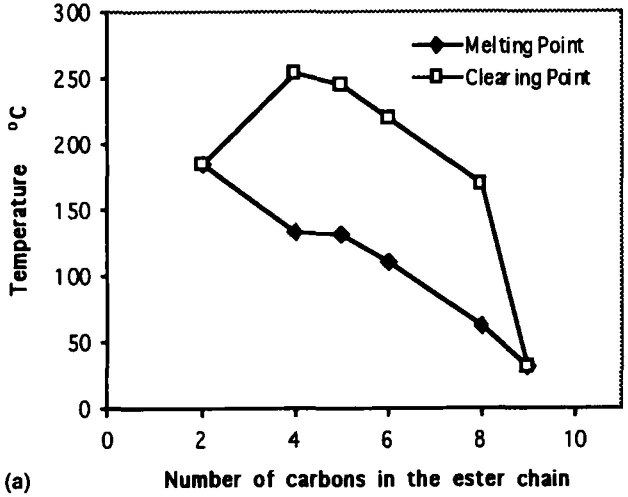

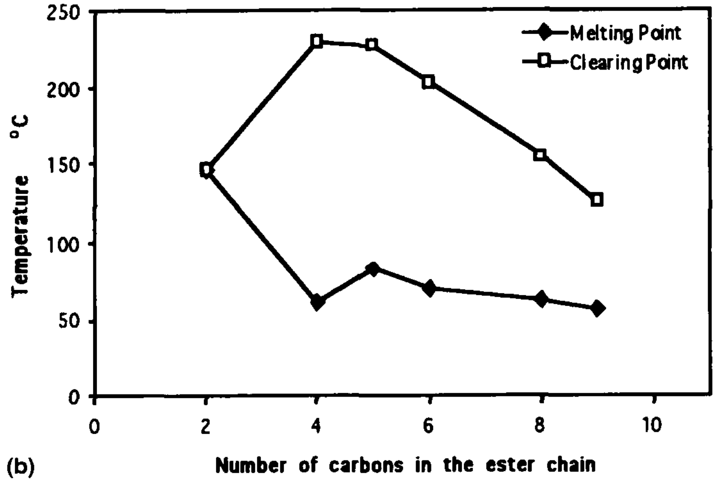

FIGURE 1 (a) Transition temperature of symmetrical mixed tail triphenylene derivatives; (b) Transition temperature of nonsysmmetrical mixed tail triphenylene derivatives.

on cooling slowly crystallizes in between 7 to −25°C. Rest all the compounds in series 1 and 2 *i.e.*, **1b–e** and **2b–f** exhibit classical textures of columnar mesophases upon cooling from the isotropic liquid. These textures are very similar to known textures for Col_h phases (D_h phases according to previously followed notation). While lower members of both the series (**1a–d** and **2a–d**) show sharp mesophase to isotropic transitions, the higher homologues give only broad peaks in DSC. Highly reversible

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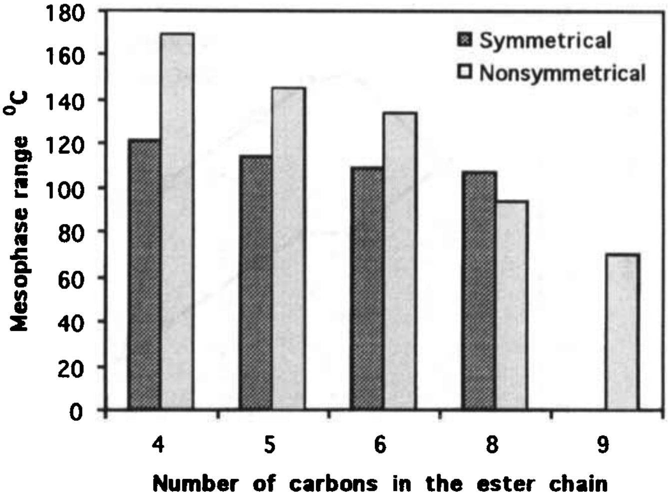

FIGURE 2 Mesophase range of symmetrical and nonsymmetrical mixed tail triphenylene derivatives.

behavior is observed at the clearing point of all the compounds and only a very small hysteresis is observed over many heating and cooling cycles. Conversely, the melting transition was found to be irreversible. Upon cooling, all mesophases supercool to room temperature. None of the members of unsymmetrial series show any sign of crystallization upon keeping at room temperature for a long period *c.a.* one month. However, all the symmetrical derivatives (**1b–e**) crystallize on annealing at room temperature for about one hour. It should be noted that assignment of a Col$_h$ phase in all the new mixed tail triphenylene derivatives was determined only by polarized optical microscopy. Detailed X-ray work has yet to be done for the full characterization.

Figures 1a and b represent the transition temperature of symmetrical and unsymmetrical triphenylene derivatives in graphical form. A glance on these graphs clearly indicates that in both the cases, the mesophase to isotropic temperature gradually decreases, as expected, on increasing the number of carbon in the ester chain. In the case of symmetrical series, when the ester chain is of nine carbons, (*i.e.*, nonyloxy), the molecule becomes non-mesomorphic. However, unsymmetrical molecule with the same chain exhibits a broad mesophase range.

Figure 2 shows a comparison of mesophase range of symmetrical and unsymmetrical triphenylene derivatives having the same number of carbons in the side chain. As can be seen from the graph, most of the unsymmetrical derivatives have larger mesophase range as compared with their symmetrical

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counterparts. From the graph it can also be observed that the mesophase range in the symmetrical series does not vary much when the number of carbons in the ester chain increases from four to eight. On the other hand, in the nonsymmetrical series it changes significantly. If we compare the mesophase range of hexapentyloxytriphenylene (Cr 69°C Col_h 122°C I, mesophase range 53°C) [6], hexapentanoyloxytriphenylene (Cr 193°C I, mesophase range 0°C) [6] and the two mixed tail triphenylene derivatives having the same number of carbons in the side chain, *i.e.*, **1c** (mesophase range 114°C) and **2c** (mesophase range 145.1°C), it is clear that in both the hybrid molecules mesophase range is significantly high.

The above results reveal a general trend in these mixed tail triphenylene derivatives. The nonsymmetric isomers have a lower temperature and broader mesophase range than the symmetric isomers. Because of the C_3 symmetry in 2,6,10-trialkanoyloxy-3,7,11-trialkoxytriphenylene derivatives, these molecules have a much greater chance of optimal packing leading to crystallization. Breaking of symmetry causes disorder and thus suppressing crystallization. Clearly, there is a strong relationship between molecular structure and mesophase stabilization.

We believe that in the columnar packing, particularly when the molecule has a bulky group in its periphery, two adjacent molecules do not exactly overlap each other but one molecule rotates itself in order to minimize steric hindrance and adopt an energetically favored staggered or anti conformation. A schematic representation of a staggered conformation is shown in Figure 3a. The second molecule may arrange itself in such a position that its peripheral chains fall in the vacant space of the first molecule (in the 'bay regions') (Fig. 3b). In Figure 4, symmetrical and nonsymmetrical molecule

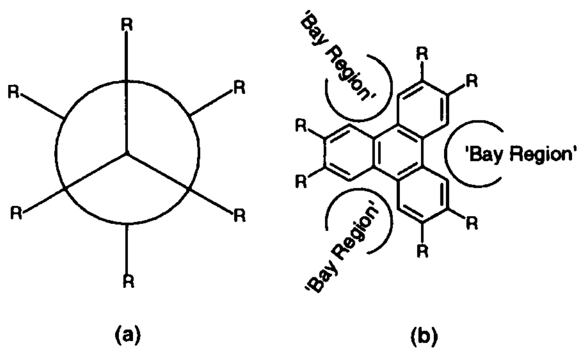

FIGURE 3 (a) Schematic representation of a staggered configuration; (b) Schematic representation of 'Bay Region' in a triphenylene molecule.

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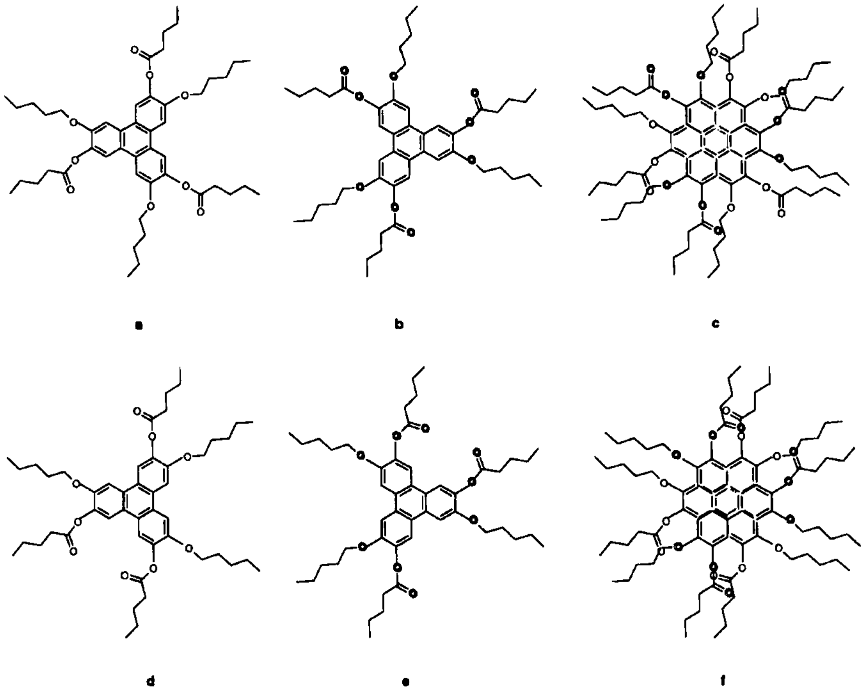

FIGURE 4 (a) Chemical structure of a symmetrical molecule **1c**; (b) **1c** was rotated by 180°; (c) Structure b was stacked over structure a; (d) Chemical structure of a nonsymmetrical molecule **2c**; (e) **2c** was rotated by 180°; (f) Structure e was stacked over structure d.

was rotated by 180° and than placed over the first molecule. Apparently in the case of symmetrical derivatives two adjacent molecules having alternative ether (planar) and ester (out of plane) groups do not experience much steric hindrance but the nonsymmetrical molecules do. This may reduce the packing efficiency of the mesogens and they do not crystallize from the neat liquid crystal phase and remain in a super-cooled columnar phase indefinitely at room temperature. The results confirm the concept that the ester linkages stabilize the columnar mesophase. Unsymmetric substitution, in addition, lowers the melting point and hinders crystallization, thus further increasing the mesophase range [12].

CONCLUSIONS

We have synthesized twelve new mixed tail triphenylene derivatives having three ether and three ester chains. These chains are attached symmetrically

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or unsymmetrically to the triphenylene core. Mixed tail triphenylene derivatives have much higher mesophase range compared to hexaether or hexaester derivatives of triphenylene. Molecules with C_3 symmetry have better chance of optimal packing and, therefore, less mesophase stabilization compared to nonsymmetric molecules. These results are very important in designing new discotic liquid crystals of desired thermal properties. Synthesis of various mixed tail triphenylene discotic liquid crystals bearing conjugative electron-withdrawing or electron-releasing, planar or out of the molecular plane substituents attached directly to the triphenylene core are currently under investigation in our laboratories.

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