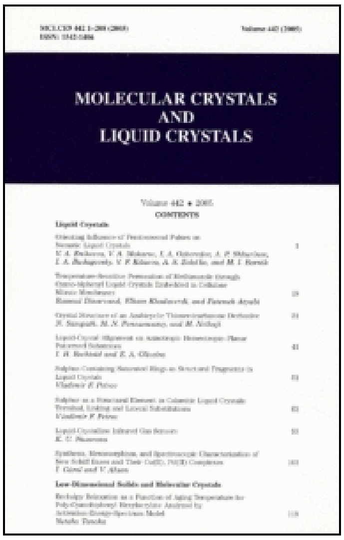

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Synthesis and Liquid-Crystalline Properties of β-Bromopentakis(Alkoxy) Triphenylene: Reactivity of $VOCl_3$, $MoCl_5$, and $FeCl_3$ as Oxidants

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Synthesis and Liquid-Crystalline Properties of *β*-Bromopentakis(Alkoxy) Triphenylene: Reactivity of $VOCl_3$, $MoCl_5$, and $FeCl_3$ as Oxidants

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We present a simple synthetic strategy leading to nonsymmetrical functionalized hexasubstituted triphenylene. Further, new β-bromopentakis(alkoxy)triphenylene was synthesized applying this strategy and reactivity of oxidizing agents such as $VOCl_3$*,* $MoCl_5$*, and* $FeCl_3$ *was investigated. The liquid-crystalline properties were studied by polarizing optical microscope (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) studies. The higher homologues exhibit a columnar hexagonal (*Col_h*) phase, whereas lower homologues also exhibit a columnar hexagonal plastic (*Col_{hp}*) phase. These mesophases are stable below and above the ambient temperature. We studied the effect of polar substitution on molecular self-assembly and found that a bromo bulky substituent at the β-position of pentakis(alkoxy)triphenylenes stabilized the intra- or intermolecular interaction between the cores to form columnar mesophases.*

Keywords Columnar; columnar hexagonal plastic; discotic liquid crystals; oxidative coupling; triphenylene

Introduction

Discotic liquid crystals (DLCs) represent a promising class of new functional materials with respect to their one-dimensional molecular structure and two-dimensional self-organization, such as photoconductivity properties. To modify the processability and mesophase behavior of such materials, functionalized cores are required as precursor molecules for molecular engineering of discotic molecules such as oligomers and polymers. One such important material is triphenylene (TP) compounds, which have a charge carrier mobility of holes (μ_+) of ca. $0.1\,cm^2\,V^{-1}\,s^{-1}$ in a helical columnar mesophase [1]. This property has created the *molecular concept* to

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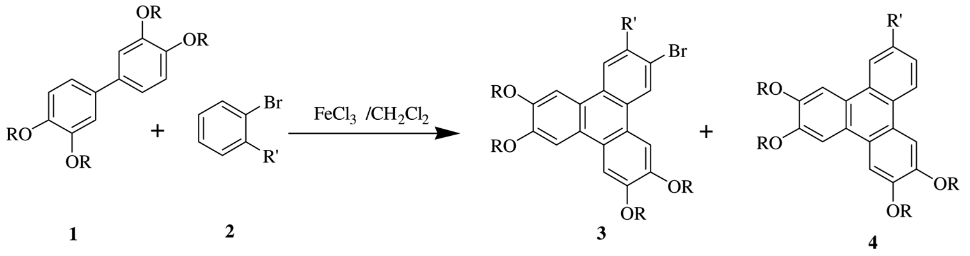
chemists in the field of DLCs [2]. Thus, the molecular concept of DLCs is mainly synthetically developed to bring the structural diversity and needs to stabilize a reliable structure-property relationship, in parallel with physical and theoretical investigations. A variety of molecular concepts have been developed such as molecular structure of the conjugated core and its symmetry, phase and transition temperature engineering by the variation of peripheral aliphatic tails, and connecting functional groups between peripheral tails and the core [3]. The potential applications of TP DLCs have led to intense activity in their synthesis and various new methods have been developed [4]. Therefore, TP-based DLCs have been considered as functional materials for applications such as photovoltaic cells and field effect transistors. The main interest comes from the high charge carrier mobilities that have been obtained for some of these materials, especially in the Col_{hp} mesophase [5].

Chloranil and $FeCl_3$ were initially used to prepare the nonmesogenic hexamethoxytriphnylene [6] by oxidative trimerization of veratrol in the presence of concentrated H_2SO_4. Thereafter, an improved method of $FeCl_3$ to prepare mesogenic hexaalkoxytriphenylene was reported by Boden *et al.* [7]. Further, $MoCl_5$ as oxidant to prepare the mesogenic triphenylene was reported by Kumar and Manickam [8]. Thereafter, $VOCl_3$ as liquid reagent, allowing milder reaction conditions and spontaneous trimerization of 1,2-dialkoxybenzene, to prepare mesogenic TP in high yield was reported by Kumar and Varshney [9].

However, electronegative moiety allows a number of functional groups to interchange reactions, opening up further variations in the molecular structures. Monofunctionalized triphenylenes are extremely important precursors for the synthesis of dimers, oligomers, and polymers and represent valuable precursors in the molecular engineering of DLCs [10]. A variety of methods and catalysts have been developed to prepare the substituted TPs but the direct method of oxidative coupling of electron-rich biphenyl and electron-deficient monofunctionalized monoalkoxybenzene has not been explored much. However, hitherto, only three oxidizing agents, $FeCl_3$, $MoCl_5$, and $VOCl_3$, are commonly used to achieve the mesogenic TP [11]. Further, these reagents have several limitations, particularly when the substitutions belong to electron-donating groups. Therefore, it is interesting to study the reactivity of these oxidants in the preparation of TP having an electronegative (polar) functional group [12]. Thus, our interest is to examine the possibility of using these three reagents to prepare the β-bromopentakis (alkoxy)triphenylene [13]. However, we have used different strategies to prepare β-bromopentakis(alkoxy)triphenylene having a bromo functional group, and it was synthesized by direct oxidative coupling to study the effect of functional group on molecular self-organization.

Results and Discussion

The key intermediates for the preparation of symmetrical ($R = R'$) and unsymmetrical ($R \neq R'$) TP-Br are 3,3′,4,4′-tetraalkoxybiphenyl and β-bromoalkoxybenzene. 3,3′, 4,4′-Tetraalkoxybiphenyl was synthesized by Ullmann coupling of 4-iodo-1,2-dialkoxybenzene, whereas β-bromoalkoxybenzene was achieved by alkylation of β-bromophenol. Through oxidative coupling with $VOCl_3/FeCl_3/MoCl_5$, a mixture having several compounds was obtained, which was separated by column chromatography as shown in Scheme 1. The chemical structure and purity of these derivatives were confirmed by the spectral data.



(a): $R = C_4H_9$, $R' = OC_4H_9$; **(b):**$R = C_5H_{11}$, $R' = OC_5H_{11}$; **(c):** $R = C_6H_{13}$, $R' = OC_6H_{13}$
(d): $R = C_7H_{15}$, $R' = OC_7H_{15}$; **(e):** $R = C_8H_{17}$, $R' = OC_8H_{17}$
(f): $R = (CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_3$, $R' = O(CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_3$
(g): $R = C_5H_{11}$, $R' = OCH_3$; **(h):** $R = C_5H_{11}$, $R' = OCH_2CH(C_2H_5)(CH_2)_3CH_3$
(i): $R = C_5H_{11}$, $R' = O(CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_3$

Scheme 1. Synthesis of β-bromopentakis(alkoxy)triphenylenes. Symmetrical: R and R′ are similar. Unsymmetrical: R and R′ are different.

$FeCl_3$ was used to prepare homologues series of TP-Br as shown in Scheme 1. Oxidative coupling of tetraalkoxybiphenyl (**1**) with monoalkoxybromobenzene (**2**) gave the target compound **3** in 60–85% yield. However, we found that $FeCl_3$ was very easy to handle compared to $MoCl_5$. It is worth mentioning here that we also carried out some of the reactions in noninert conditions successfully. $MoCl_5$ also formed the product but the yield was 30–45%. TP-Br was not achieved by $VOCl_3$. Details are given later in this section.

Liquid-Crystalline Properties

In this study, we have synthesized nine TP derivatives. All the derivatives exhibit liquid-crystalline phases. The transition temperatures and associated enthalpies obtained from differential scanning calorimetry (DSC) thermograms are summarized in Table 1.

Table 1. Thermal behavior of compound **3**

Compd. 3	Heating scan	Cooling scan
a	Col$_{hp}$ 68.8 (1.3) Col$_h$ 178.9 (10.1) I	I 177.6 (9.8) Col$_h$ 62.1 (1.7) Col$_{hp}$
b	Col$_{hp}$ 17.6 (1.9) Col$_h$ 167.2 (7.6) I	I 165.6 (6.7) Col$_h$
c	Cr 56(32.7) Col$_h$ 149.2 (3.0) I	I 147.3 (0.7) Col$_h$ −3.5 (23.5) Cr
d	Cr 33(15.2) Col$_h$ 136.5 (3.3) I	I 134.3 (3.6) Col$_h$ −10.0 (16.8) Cr
e	Cr 35.5 (2.5) Col$_h$ 129.9 (1.7) I	I 126.3 (3.8) Col$_h$ −3.3 (25.5) Cr
f	Col$_h$ 98.0 (9.6) I	I 96.0 (9.2) Col$_h$
g	Cr 108.2 (48.0) Col$_h$ 160.4 (7.0) I	I 158.7 (6.0) Col$_h$ 53 g
h	Col$_h$ 133.6 (6.9) I	I 132.0 (6.8) Col$_h$
i	Col$_h$ 135.0 (4.5) I	I 132.0 (5.0) Col$_h$

Cr = crystal; Col$_h$ = columnar hexagonal; Col$_{hp}$ = columnar hexagonal plastic; g = glassy transition; I = isotropic liquid.

Temperatures are given in °C and enthalpies (in parentheses) are given in kJ mol^{-1}.

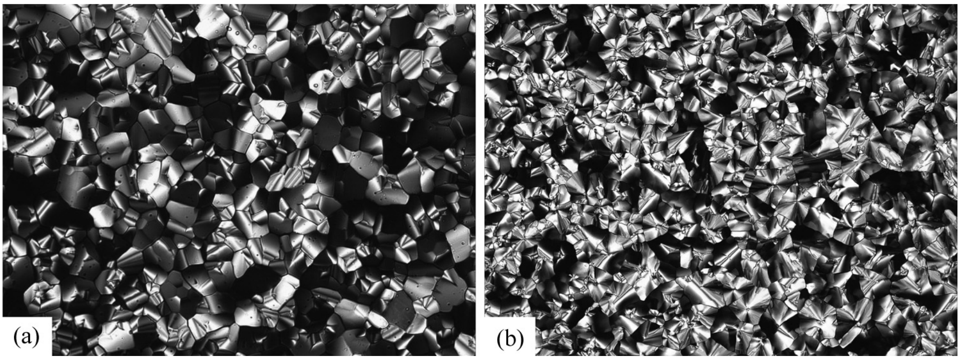


Figure 1. The selected optical textures of compounds **3e** and **3f** obtained on cooling from isotropic liquid; (a) $\mathrm{Col_h}$ phase of **3e** at 67°C and (b) $\mathrm{Col_h}$ phase of **3f** at RT.

The compound **3a** showed the $\mathrm{Col_{hp}}$ phase with a focal conic (plate-like) texture, which changed to a focal conic texture of $\mathrm{Col_h}$. On cooling, both the mesophases appeared at their respective temperatures and $\mathrm{Col_{hp}}$ was not crystallized at room temperature (RT). Compound **3b** [13] showed the focal conic texture of the $\mathrm{Col_h}$ phase, which was retained until RT. The $\mathrm{Col_{hp}}$–$\mathrm{Col_h}$ transition was not observed in higher members of this series. Compound **3(c–e)** showed the $\mathrm{Col_h}$ phase, which was crystallized above the ambient temperature. The observed texture of the $\mathrm{Col_h}$ phase is shown in Fig. 1a. Compound **3f** with branched peripheral chains showed the $\mathrm{Col_h}$ phase at RT and glassy or crystallization transition was not observed by DSC scans until −55°C; see Fig. 1b.

Compound **3g** showed the $\mathrm{Col_h}$ phase; on cooling the mesophase changed to a glassy state. Further, compounds **3h** and **3i** exhibited the $\mathrm{Col_h}$ phase below and above RT. A graphical representation of the mesophase range is shown in Fig. 2.

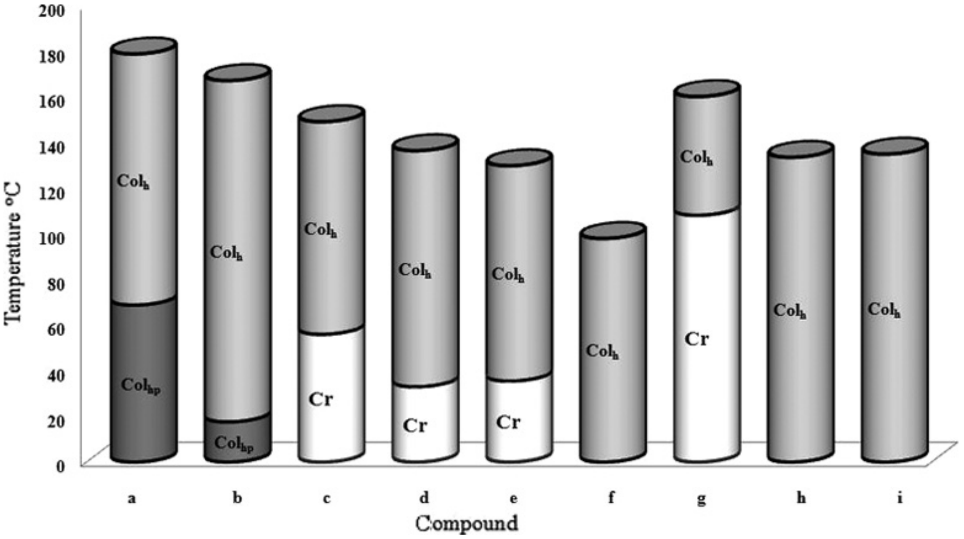
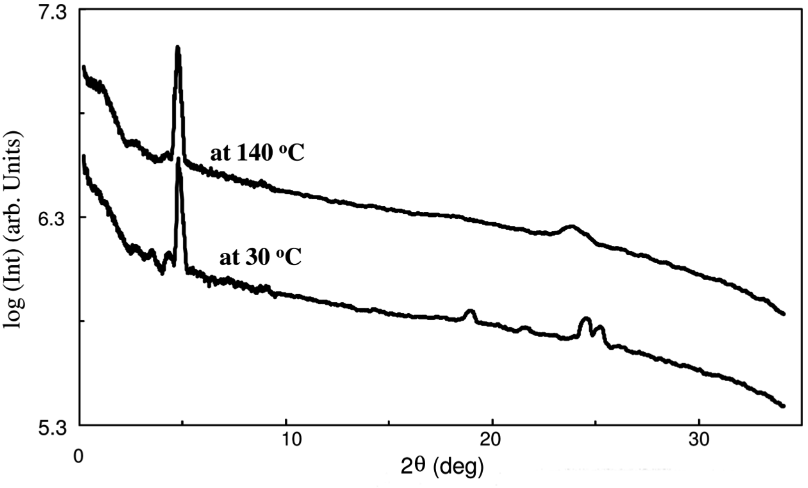


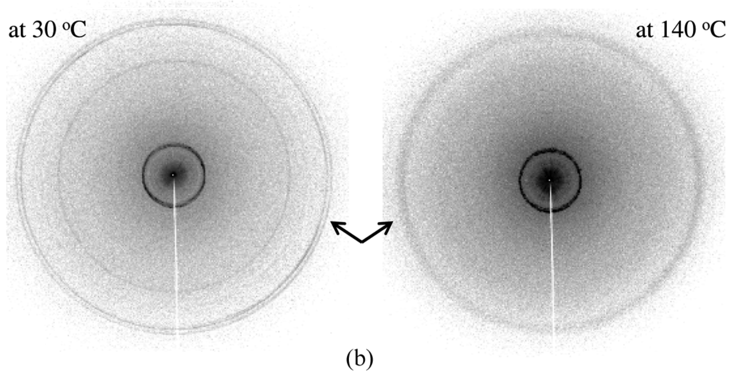
Figure 2. Graphical representation of the thermal ranges of mesophases of *β*-bromohexakis (alkoxy)triphenylenes.

X-ray Diffraction Studies

For samples **3a, 3f**, and **3i**, X-ray diffraction (XRD) measurements were carried out at a required temperature. Different diffraction patterns obtained for the compounds **3(a & f)** and its one-dimensional intensity vs. 2$\boldsymbol{\theta}$ profile derived by integrating over the entire χ (0–360°) range are shown in Figs. 3 and 4. The results of these investigations are given in Table 2. The XRD scans of compound **3a** obtained at 140°C showed a sharp peak at the small angle region having the intercolumnar distance (lattice spacing) 19.3 Å and a diffuse peak in the wide-angle region that corresponds to the alkyl chains. A relatively sharp but still diffuse peak corresponds to the core–core correlation at $2\boldsymbol{\theta} \sim 25$ that gives the intracolumnar molecular distance 3.6 Å (Fig. 3). The obtained data suggested the $\mathrm{Col_h}$ mesophase. The different diffraction pattern was obtained at 30°C. The small angle region is similar to that at 140°C, whereas the wide-angle region shows few peaks being different from that at 140°C. The core–core peak, which is single in the $\mathrm{Col_h}$ phase, splits into two peaks (sawtooth shape) at 3.51 and 3.42 Å (Fig. 3). We determined that these reflections correspond to the 2D hexagonal lattice. Thus, the overall features determined are



(a)



(b)

Figure 3. X-ray diffraction pattern of compound **3a**: (a) X-ray diffraction intensity vs. 2θ; (b) obtained from 2D pattern at 140°C (left side) and 30°C (right side).

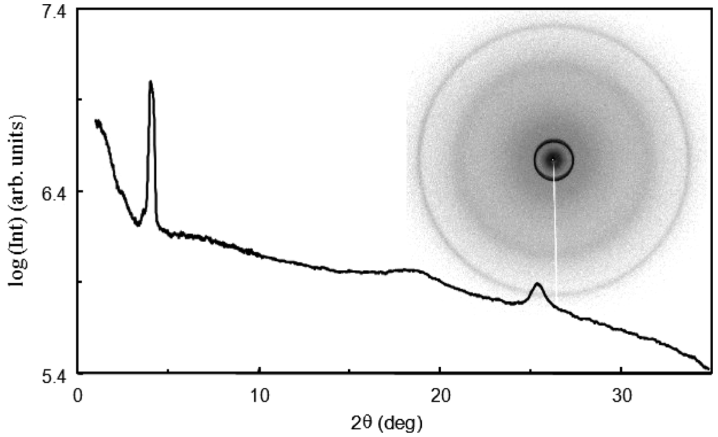


Figure 4. Intensity vs. 2θ of compound **3f** and corresponding 2D diffraction pattern obtained at RT (25°C).

Table 2. Transition enthalpy for the isotropic → Col_x/Col_h and $Col_h \rightarrow Col_{hp}$ transformation, disc diameter, lattice parameters, and core–core distance for liquid-crystalline phases of compound **3**

Compound	Phase and parameters	$\Delta H/kJ\,mol^{-1}$	d spacing/Å	d_{inter}/Å
a	Col_h			
	140°C	9.8	16.74	19.33
	Alkyl		4.63	
	Core–core		3.60	
	Col_{hp}			
	30°C	1.7	16.58	19.17
	Alkyl		4.57	
	Core–core		3.51	
	Core–core		3.42	
f	Col_h			
	80°C	9.2	23.06	26.63
	Alkyl		4.93	
	Core–core		3.57	
	Col_h			
	25°C		23.12	26.72
	Alkyl		4.81	
	Core–core		3.49	
i	Col_h			
	100°C	5.0	19.2	22.17
	Alkyl		4.72	
	Core–core		3.58	
	Col_h			
	25 °C		17.89	20.66
	Alkyl		4.60	
	Core–core		3.51	

consistent with the $\mathrm{Col_{hp}}$ mesophase in which only minor positional fluctuations of the molecules are possible [14].

Compounds **3f** and **3i** showed the similar diffraction pattern at RT and elevated temperatures (Fig. 4). The intercolumnar distance of compound **3f** was calculated to be 26.6 Å and the core–core distance obtained was 3.53 Å. In the case of compound **3i**, intercolumnar distance at 100°C was 22.1 Å. Upon cooling, the lattice parameter decreased slightly to 20.6 Å at 25°C.

Discussion and Effect of Polar Substitution

We utilized three oxidizing agents, $FeCl_3$, $MoCl_5$, and $VOCl_3$, to try to achieve TP-Br and found that no product was formed using $VOCl_3$ as oxidant even in different reacting conditions such as temperature and concentration of the reagent and solvents. Interestingly, we found that chlorinated precursors were achieved [11]. Further, TP-Br was achieved as a minor product by $MoCl_5$ and the yield was varied by 30–45%. The major product was compound **4**. However, under various reaction conditions we could not achieve TP-Br as a major product. We achieved the synthesis of these molecules by oxidative coupling and found that $FeCl_3$ was a better oxidant for TP-Br. However, $MoCl_5$ was more appropriate for indo substituted TP [11,15]. Thus, the nature of the electron-deficient moiety, such as atomic radii and electron reactivity, also affects the reactivity of these reagents.

The structure-property relationship of compound TP-Br with monohydroxypentakis(butyloxy)triphenylene (TP-OH) and compound **4** [13,16] was studied. The compounds **TP-OH** and **4** are nonmesogenic and all the bromo/iodo group–substituted TP compounds are mesogenic. To discuss these differences and establish the structure-property relationship, we calculated chemical structures with minimized energy by an MM2 energy minimization technique; the free space in the bay region is shown in Fig. 5.

Apparently compound **3a** and TP-OH have similar free space in the bay region as shown in Figs. 5a and 5b. Compound **3** with a polar group such as bromo and iodo preferred to establish weak intermolecular interactions, preventing closed molecular packing. Thus, the molecules have a greater chance of fluctuating packing, which leads to a mesophase with energetically favored conformation. The second molecule may arrange itself in such a position that its peripheral chains fall in the vacant space of the first molecule and induce the intermolecular interaction to show the mesophase. This could not be true in the case of compound TP-OH. As shown in Fig. 5c, the enhancement of the free space in the bay region of compound **4** stabilizes the stronger intermolecular interaction and do not experience much molecular steric hindrance. As a result, molecules have a greater chance of optimal packing to lead the crystalline phase. However, the concept that a bulky substituent stabilized the mesophase is supported by the nonmesogenic behavior of compound TP-OH.

Generally, the decreasing electronegativity with increasing covalent radii of the polar moiety increased the melting/clearing temperature, whereas decreasing chain length increased the melting temperature. Compound **3a** and TP-Ia [15] show clearing temperature at 178.9°C and 176.5°C, respectively. But the temperature range of the highly ordered mesophase increased with decreasing covalent radii (iodo → bromo). However, this suggested that the aliphatic side chains of the minimum length are necessary to reduce core–core interaction and induce enough flexibility into the self-assembly to decrease π–π interaction sufficiently for the formation of

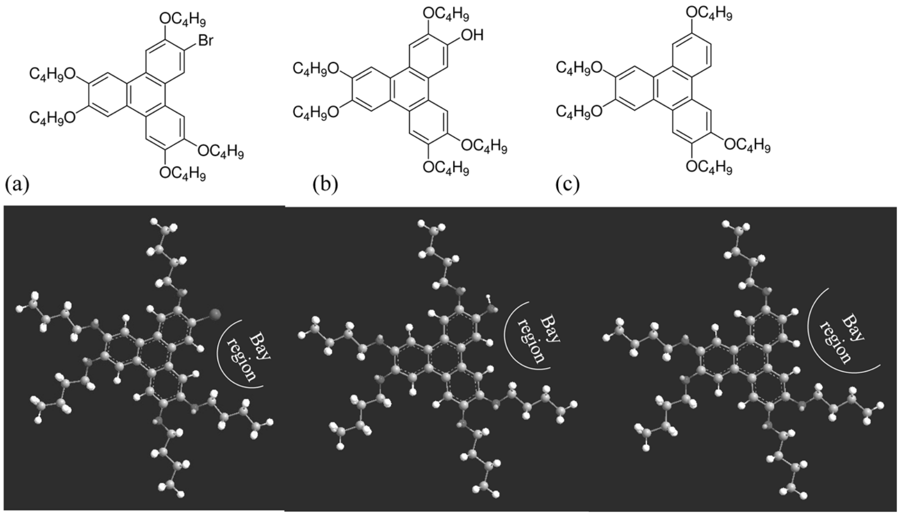


Figure 5. Chemical structure and MM2 energy minimized structures for space filling model that show the bay regions of (a) compound **3a**, (b) compound TP-OH having butyl alkoxy peripheral chains, and (c) compound **4a**.

a columnar mesophase. That could be the reason why disc-shaped molecules with short peripheral chains are preferred to exhibit the highly ordered columnar mesophase such as $\mathrm{Col_{hp}}$. Therefore, intercolumnar distance also plays an important role in the formation of the $\mathrm{Col_{hp}}$ mesophase. This is an important factor to charge carrier properties. Recently, the highest ever charge carrier mobility value for any liquid-crystalline TP system in the $\mathrm{Col_{hp}}$ phase was reported [17].

Summary

We have prepared a series of β-bromopentakis(alkoxy)TP mesogens by oxidative coupling that could be a versatile method compared to previously reported methods, and reactivity of $FeCl_3$, $MoCl_5$, and $VOCl_3$ as oxidant was studied to obtain the maximum yield. TP-Br could not be formed by VOCl3, whereas TP-Br was formed by $MoCl_5$ in low yield (minor product) and was tricky to separate from the product. TP-Br was formed by $FeCl_3$ as a major product, which was easily separated from the other side products. Indeed, several β-bromopentakis(alkoxy)-TP derivatives were prepared by $FeCl_3$ by a direct method. The methodology provides an easy, high-yielding process for the preparation of various bromo substituted triphenylene discotics. The longer peripheral alkyl chains exhibit the $\mathrm{Col_h}$ phase, whereas shorter peripheral alkyl chains exhibit the $\mathrm{Col_{hp}}$ mesophase below and above the ambient temperature. This clearly shows that the shorter peripheral alkyl chains can reduce molecular steric hindrance to exhibit the ordered $\mathrm{Col_{hp}}$ mesophase.

Experimental

General

All the starting chemicals and solvents were employed commercially and were used without any further purification. Column chromatographic were performed on silica gel (230–400 and 120–200 mesh). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F_{254}). Mass spectra were recorded on a JEOL J600H spectrometer in FAB^+ mode using an *m*-nitrobenzyl alcohol (NBA) matrix. Nuclear magnetic resonance (NMR) spectra were recorded on a 200- or 400-MHz Bruker machine. All chemical shifts are reported in δ units downfield from Me_4Si, and J values are given in Hz. The phase transition temperatures of these molecules were observed by using a polarizing optical microscope (POM; Leica DMLP or Olympus BX51), equipped with a hot stage (Mettler FP82HT), controlled by a central processor (Mettler FP90), and measured by a DSC (DSC-7 or Diamond Perkin-Elmer). XRD measurements were performed using an image plate detector (MAC Science DIP1030). Unoriented samples contained in sealed Lindemann glass capillaries were irradiated with Cu Kα rays obtained from a sealed-tube generator (Enraf-Nonius FR 590) in conjunction with double-mirror focusing optics.

General Procedure for the Preparation of (β-Bromopentakis(Alkoxy)-TP (3)

3,3′,4,4′-Tetraalkoxybiphenyl (1.1 mmol) and β-bromoalkoxybenzene (1.5 mmol) were placed into a round-bottom flask and the mixture was deoxygenated. Fifteen multiliters of dry CH_2Cl_2 as a solvent was added under the anhydrous conditions. The bright $FeCl_3$ (3 mmol) was added in portions. The mixture was stirred at RT in an atmosphere of dry argon for 30 min, after which it was quenched with chilled MeOH. The solution was diluted with water and was extracted with CH_2Cl_2 (30 mL × 3) and washed with brine, which was concentrated and purified by column chromatography (×3) over silica gel using hexane/dichloromethane as eluent to give desired β-bromopentakis(alkoxy)TPs as a white solid in 60–84%. Finally, it was recrystallized from diethyl ether-methanol to afford a white solid or semi-solid.

(a) β-Bromo-3,6,7,10,11-pentakis(butoxy)TP. Yield: 84%, ^{1}H NMR: δ 8.59 (s, 1H, Ar), 7.86 (s, 1H, Ar), 7.81 (m, 4H, Ar), 4.23 (t, 10H, $J = 6$, $-OCH_2-$), 1.93 (m, 10H, $-OCH_2CH_2-$), 1.62 (m, 10H, $-CH_2-$), 1.04 (t, 15H, $J = 7.3$, $-CH_2CH_3$). ^{13}C NMR: 153.6, 150, 149.4, 149.1, 148.9, 129.3, 127.7, 124.8, 124.1, 123.2, 122.8, 122.7, 112.3, 107.8, 107.3, 106.9, 106.4, 105.7, 69.6, 69.3, 69.2, 69.0, 31.5, 31.4, 31.3, 19.4,13.9. MS m/z (FAB^+): 668 [M^+].

(b) β-Bromo-3,6,7,10,11-pentakis(pentyloxy)TP. Yield: 78%, ^{1}H NMR: δ 8.56 (s, 1H, Ar), 7.83 (s, 1H, Ar), 7.78 (m, 4H, Ar), 4.22 (m, 10H, $-OCH_2-$), 1.92 (m, 10H, $-OCH_2CH_2-$), 1.53 (m, 20H, $-CH_2-$), 0.97 (t, 15H, $J = 6.9$, $-CH_2CH_3$). MS m/z (FAB^+): 738 [M^+].

(c) β-Bromo-3,6,7,10,11-pentakis(hexyloxy)TP. Yield: 75%, ^{1}H NMR: δ 8.59 (s, 1H, Ar), 7.86 (s, 1H, Ar), 7.81 (m, 4H, Ar), 4.23 (m, 10H, $-OCH_2-$), 1.94 (m, 10H, $-OCH_2CH_2-$), 1.54 (m, 30H, $-CH_2-$), 0.95 (t, 15H, $J = 6.9$, $-CH_2CH_3$). MS m/z (FAB^+): 808 [M^+].

(d) β-Bromo-3,6,7,10,11-pentakis(heptyloxy)TP. Yield: 65%, ^{1}H NMR: δ 8.58 (s, 1H, Ar), 7.85 (s, 1H, Ar), 7.79 (m, 4H, Ar), 4.25 (t, 10H, $J = 5.5$, $-OCH_2-$), 1.94 (m, 10H, $-OCH_2CH_2-$), 1.54 (m, 40H, $-CH_2-$), 0.91 (t, 15H, $J = 6$, $-CH_2CH_3$). ^{13}C NMR: 153.6, 150, 149.4, 149.1, 148.9, 129.3, 127.8, 124.9, 124.1, 123.2, 122.9,

122.8, 112.3, 107.8, 107.4, 106.4, 105.8, 69.9, 69.8, 69.5, 69.3, 31.8, 29.5, 29.4, 29.2, 29.1, 26.1, 22.6,14. MS m/z (FAB^+): 879 [M^+].

(e) β-Bromo-3,6,7,10,11-pentakis(octyloxy)TP. Yield: 65%, ^1H NMR: δ 8.58 (s, 1H, Ar), 7.85 (s, 1H, Ar), 7.8 (m, 4H, Ar), 4.23 (m, 10H, $-OCH_2-$), 1.94 (m, 10H, $-OCH_2CH_2-$), 1.54 (m, 50H, $-CH_2-$), 0.90 (m, 15H, $-CH_2CH_3$). ^{13}C NMR: 153.6, 150, 149.4, 149.1, 148.8, 129.3, 127.7,124.8, 124.1, 123.2, 122.8, 122.7, 112.3, 107.8, 107.4, 106.9, 106.3, 105.8, 69.9, 69.8, 69.5, 69.3, 31.8, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7, 14. MS m/z (FAB^+): 949 [M^+].

(f) β-Bromo-3,6,7,10,11-pentakis(3,7-dimethyl-octyloxy)TP. Yield: 55%, ^1H NMR: δ 8.59 (s, 1H, Ar), 7.86 (s, 1H, Ar), 7.8 (m, 4H, Ar), 4.27 (m, 10H, $-OCH_2-$), 2.0 (m, 5H, $-CHCH_3$), 1.77 (m, 10H, $-OCH_2CH_2$) 1.56 (m, 50H, $-CH_2-$), 0.89 (m, 30H, $-CH_2CH_3$, $CHCH_3$). ^{13}C NMR: 153.5, 149.4, 149.3, 149.0, 148.7, 129.3, 127.7, 124.8, 124.1, 123.1, 122.7, 112.2, 107.5, 107.1, 106.7, 106.1, 105.6, 68.1, 67.7, 67.6, 39.2, 37.4, 36.6, 36.1, 30.0, 27.9, 24.7, 22.6, 19.7. MS m/z (FAB^+): 1089 [M^+].

(g) β-Bromo-3-methoxy-6,7,10,ll-tetrakis(pentyloxy)TP. Yield: 77%, ^1H NMR: δ 8.57 (s, 1H, Ar), 7.86 (s, 1H, Ar), 7.79 (m, 4H, Ar), 4.23 (t, 8H, $J = 6.5$, $-OCH_2-$), 4.11 (s, 3H, $-OCH_3$), 1.95 (t, 8H, $J = 6.4$, $-CHCH_2$), 1.47 (m, 16H, $-CH_2-$), 0.97 (t, 12H, $J = 6.8$, $-CH_2CH_3$). ^{13}C NMR: δ 156.0, 150.2, 149.5, 149.2, 148.9, 134.4, 127.8, 124.2, 122.6, 107.2, 106.8, 106.2, 104.5, 69.8, 69.4, 56.4, 29.0, 22.5, 14.0. 14.0, 22.5, 29.0, 56.4, 69.4, 69.8, 104.5, 106.2, 106.8, 107.2, 122.6, 124.2, 127.8. MS m/z (FAB^+): 682 [M^+].

(h) β-Bromo-3-(2-ethyl-hexyloxy)-6,7,10,ll-tetrakis(pentyloxy)TP. Yield: 64%, ^1H NMR: δ 8.58 (s, 1H, Ar), 7.85 (s, 1H, Ar), 7.8 (m, 4H, Ar), 4.23 (m, 8H, $-OCH_2-$), 4.15(d, *2H*, $J = 5.4$, $-OCH_2CH$) 1.94 (m, 9H, $-OCH_2CH_2-$, & CH_2CHCH_2), 1.54 (m, 24H, $-CH_2-$), 0.90 (m, 18H, $-CH_2CH_3$). ^{13}C NMR: δ 153.8, 150.0, 149.4, 149.4, 149.1, 148.8, 129.3, 127.7, 124.9, 124.0, 123.2, 122.9, 122.8, 112.4, 107.9, 107.4, 106.9, 106.3, 105.4, 69.8, 69.5, 69.3, 39.5, 30.7, 29.2, 29.1, 29.0, 28.3, 24.0, 23.0, 22.5, 14.0, 11.3. MS m/z (FAB^+): 780 [M^+].

(i) β-Bromo-3-(3,7-dimethyl-Octyloxy)-6,7,10,11-tetrakis(pentyloxy)TP. Yield: 68%, ^1H NMR: δ 8.54 (s, 1H, Ar), 7.82 (s, 1H, Ar), 7.76 (m, 4H, Ar), 4.25 (m, 10H, $-OCH_2-$), 1.95 (m, 10H, $-OCH_2CH_2-$), 1.56 (m, 10H, $-CH_2-$), 1.39 (m, 17H, $-CH_2-$ & CH), 0.98 (m, 18H, $-CH_2CH_3$ & $CHCH_3$). ^{13}C NMR: δ 22.5, 24.7, 27.9, 28.3, 29.0, 29.1, 29.9, 36.0, 37.3, 39.2, 67.7, 69.2, 69.3, 69.7, 105.5, 106.1, 106.7, 107.1, 107.6, 112.1, 122.6, 122.7, 123.0, 124.0, 124.7, 127.6, 129.2, 148.7, 148.9, 149.3, 149.9, 153.5. MS m/z (FAB^+): 808 [M^+].

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