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Influence of acetylene-containing peripheral chains on the mesomorphic properties of triphenylene-based liquid crystals

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Three series of novel acetylene-containing triphenylene-based liquid crystals have been prepared. One class of material is symmetrical with the acetylenic unit located at the terminus of a peripheral alkynyloxy chain in a peripheral position at the terminus of an alkoxy chain. These symmetrical hexa-substituted materials possess high melting points which renders mesomorphism monotropic. A second class comprises materials where only one of the six peripheral units contains a terminal alkyne chain. The asymmetry confers relatively low melting points and an enantiotropic hexagonal columnar mesophase is exhibited for all materials, albeit to a lower temperature than the known parent systems. The third series of materials also comprises unsymmetrical structures, here containing one acetylenic unit conjugated with the triphenylene core and five alkoxy chains. This third series of materials show enhanced π–π interactions and enhanced space-filling effects of the acetylenic unit close to the core which enhance mesophase stability markedly over the hexaalkoxy analogues. This result shows that rigidity of peripheral chains, as opposed to molecular symmetry, is the significant factor for the reduction of mesophase stabilities.

Keywords: discotic; triphenylene; mesophase enhancement; acetylene; steric

1. Introduction

Over 30 years of discotic liquid crystal research has revealed more than 50 core units that can give rise to columnar-style mesomorphism (*1–3*). However, of all of the disc-shaped core units that can give rise to mesomorphic behaviour, triphenylene remains, to date, the most widely investigated (*3*). The wide-ranging investigation of triphenylene-based discotic materials is due to several different factors: the triphenylene core is readily accessible through well-established synthetic routes, the triphenylene core is excellent at conferring liquid crystalline properties, and hexa-substituted derivatives of triphenylene (especially ethers and esters) have a strong tendency to form ordered columnar mesophases (*3*, *4*). Triphenylene-based discotics are, therefore, extremely interesting structures to investigate, since columnar mesophases are of great technological importance because of their ability to form a one-dimensional pathway for conduction, which gives such materials excellent scope to act as semiconductors or photoconductors (*4–8*). Thus, it is essential that structure–property relationships in discotic liquid crystals in general, and in triphenylene-based materials in particular, are fully explored.

Triphenylene-based materials containing an acetylenic unit are interesting to investigate, since the acetylene unit is polarisable and possesses considerable electron density. This unique feature of the acetylene bond could exert significant influence on the mesomorphic properties of a triphenylene-based structure, since the π-system of the acetylene unit could interact with acetylene-containing chains on other molecules or the triphenylene core of other molecules, enhancing core–core interactions and thus enhancing phase stability. In addition, the enhanced π-system created by the incorporation of the acetylenic unit would also be expected to enhance the conductivity of the mesophase.

The acetylenic unit, in addition to the significant electronic effects, also exerts a significant steric and space-filling presence due to the bulky nature of the large cylindrical bonds, the effect of which upon a columnar mesophase is expected to be highly significant, as has been reported previously (*9*) with branched alkoxy chains.

Triphenylene-based compounds containing acetylenic units are known; however, to date, all such examples of acetylene-containing triphenylenes have the acetylenic unit conjugated with the triphenylene core, as in compounds **3**–**6**, for example (*10*, *11*).

These known acetylene-containing compounds exclusively exhibit the nematic discotic mesophase in compounds such as **3** and **4**, since the steric influence of the large acetylenic unit and benzene ring prevents columnar packing. The extension of the central disc by the space filling effect of the acetylene and benzene ring units, whilst preventing columnar packing, extend the overall disc shape, thus increasing the area of

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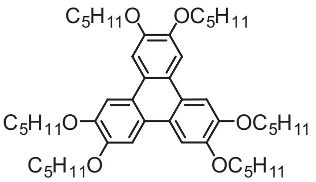
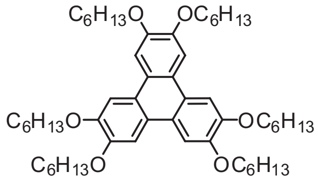
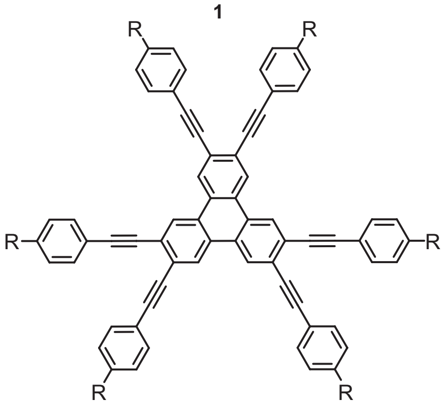


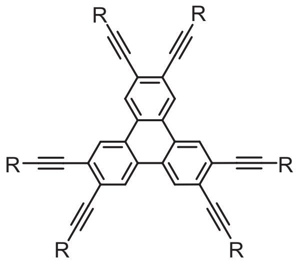
Cr 69 Col_h 122 I
1



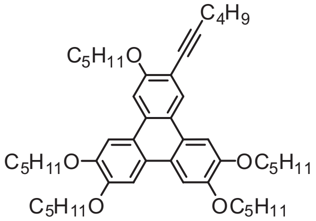
Cr 67.6 Col_h 100.1 I
2



3 R = C_5H_{11}, Cr 156.8 N_D 237.1 I
4 R = C_7H_{15}, Cr 122.0 N_D 176.2 I



5 R = C_5H_{11}, oil
6 R = C_8H_{17}, Cr 41 I



Cr 44 Col_h 157 I
7

interaction, and thus such compounds give rise to the discotic nematic phase. Without the additional benzene rings to extend the core, compounds **5** and **6** lack the enhanced disc size of compounds **3** and **4**, but still possess the steric effect of the six acetylene bonds which prevent columnar packing, and hence no mesomorphism is exhibited (*10*). Thus, the inversion of such a structure, positioning the acetylenic unit on the periphery of the molecule, may permit the beneficial effects of the acetylenic unit (e.g. enhanced space-filling effects) to be exhibited with minimal steric influence from the unit to disrupt the columnar mesomorphism that is often generated by hexaalkoxytriphenylene architectures.

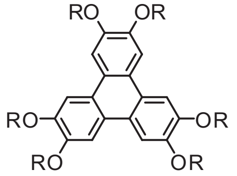
To date, only the symmetrical analogues of compounds such as **5** and **6** have been investigated, with the singular exception of compound **7**, which exhibited a depressed melting point and enhanced clearing point relative to compound **1** (*10*, *12*). In our previous investigations it has been demonstrated how such modification of a single peripheral unit (as opposed to all six peripheral units) of a hexaalkoxytriphenylene structure often permits the retention of the columnar mesophase, which is often owing to a reduction in steric factors due to the presence of fewer bulky units. This is exemplified by compound **7**, whereby the modification of a single peripheral chain (relative to compound **1**) has permitted retention of the mesophase, whereas modification of all six peripheral units, such as in compounds **5** and **6**, has destroyed mesophase stability. Thus, the modification of the HAT6 (**2**) structure by introducing one acetylene-containing chain has been investigated with the expectation that the reduction in steric factors by only introducing one bulky and antagonistic (due to π-electron repulsion) unit will permit the generation of a columnar mesophase, whilst the space-filling and possible enhanced π–π interactions introduced by the acetylenic unit will enhance the columnar phase stability relative to the parent system (**2**).

2. Results and discussion

Table 1 reveals that neither compounds **8** or **9** are mesogenic which is not surprising given the high melting points. However, on rapid cooling compound **8** does exhibit a transient monotropic Col_h mesophase (see Figure 1). Although the temperature that the transient monotropic phase exhibited by compound **8** could not be recorded accurately, because crystallisation of the material is induced by the monotropic phase transition, and this occurs at 113.4°C. Despite the melting point of compound **9** being lower than that of compound **8**, no mesophase is observed, because of the reduced rigidity of longer chains which is known to reduce clearing temperatures (compare compounds **1** and **2**).

Comparing the melting points of compounds **8** and **9** with their hexaalkoxy counterparts HAT5 (**1**, Cr 69 Col_h 122 I) (*13*) and HAT6 (**2**, Cr 67.6 Col_h 100.1 I) (*9*), reveals that the melting points of **8** and **9** are higher, with a difference of approximately 50–60°C. This enhanced melting point of the acetylenic-containing species is due to the increased molecular rigidity of compounds **8** and **9**, and the space-filling effect caused by the high electron density of the acetylenic unit. Whilst the melting points of compounds **8** and **9** have been enhanced when compared with their hexaalkoxy counterparts, the columnar mesophase stabilities have not been affected in the same manner. This disparity is not unexpected, since melting points and columnar phase stabilities are not affected to the same degree by space filling and steric effects. A typical interdisc distance for hexaalkoxy triphenylene moieties in the columnar phase is approximately 3.6 Å (*14*), thus the steric effect of the large cylindrical acetylenic bonds will disrupt molecular packing and hence reduce columnar phase stability.

Table 1. Transition temperatures of symmetrical hexa-substituted triphenylenes with terminal acetylenic peripheral chains.



		Transition temperatures (°C)		
Compound	*R*	Cr		I
8	$-(CH_2)_3-\equiv C\text{-}H$	•	130.2	•
9	$-(CH_2)_4-\equiv C\text{-}H$	•	120.9	•

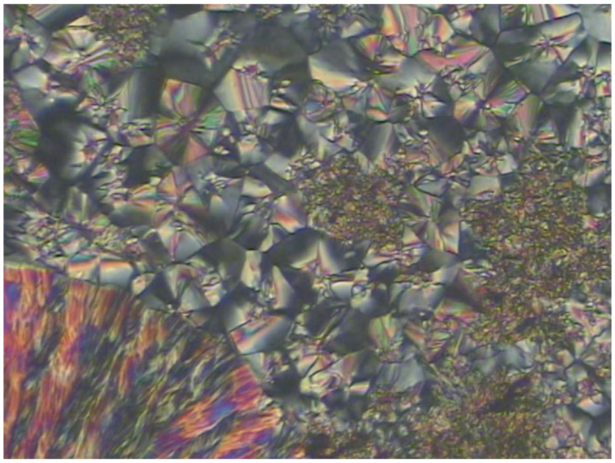
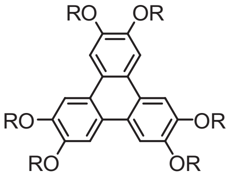


Figure 1. Transient monotropic Col_h mesophase exhibited by compound **8**.

Whilst this research was being undertaken, work was published by Cammidge, Beddall and Gopee which contained similar symmetrical structures, however containing terminal alkenes rather than alkynes (*15*).

As can be observed from the data in Table 2, compounds **10** and **11**, which are comparable to compounds **8** and **9** from Table 1, have depressed melting and clearing temperatures when compared with their symmetrical counterparts HAT5 (**1**, Cr 69 Col_h 122 I) (*13*) and HAT6 (**2**, Cr 67.6 Col_h 100.1 I) (*9*). This depression of melting and clearing temperatures is opposite to the effect of the terminal acetylenes that are displayed in Table 1, whereby the melting points have increased. This difference in the behaviour is interesting, since the terminal units are similar it may have been expected that they would exert a similar influence. However, triphenylene-based compounds containing terminal alkenes appear to resist molecular packing, whilst triphenylene-based compounds containing terminal alkynes experience enhanced intermolecular attractions

Table 2. Symmetrical triphenylenes with terminal alkenes (*15*).



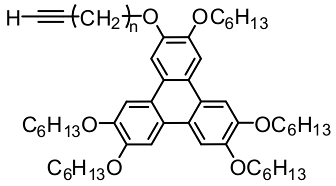
		Transition temperatures (°C)				
Compound	*R*	Cr		Col_h		I
10	$-(CH_2)_3CH{=}CH_2$	•	62	•	95	•
11	$-(CH_2)_4CH{=}CH_2$	•	64	•	92	•

due to increased alkoxy chain rigidity and increased space-filling effects, which offsets the steric effect of the acetylenic unit. This is not surprising since there is much evidence that alkene-containing chains tend to lower melting points, yet alkyne-containing chains tend to give high melting points (*16*).

In order to better compare the effects of the terminal acetylene group on mesophase morphology and stabilities, the unsymmetrical compounds (**12**–**15**) (shown in Table 3) were synthesised where five conventional hexyloxy chains are present with only one terminal alkynyloxy chain making up the six peripheral chains. Hence, these novel compounds could be compared with the entirely symmetrical HAT6 (**2**) and the unsymmetrical analogues (compounds **16**–**22**) shown in Table 4 (*9*).

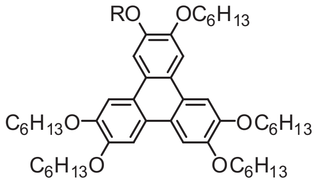
Table 3 reveals that the melting points of compounds **12**–**15** are all significantly reduced when compared with the parent compound HAT6 (**2**, Cr 67.6 Col$_h$ 100.1 I), which is not unexpected, due to the loss of symmetry. Indeed, this effect has been noted previously with unsymmetrical triphenylenes when simple alkoxy chains are present (see Table 4) (*9*). However, it is interesting to note that the melting points of these novel unsymmetrical terminal-acetylene containing materials are lower than their known unsymmetrical non-acetylene analogues (see Table 4) owing to the significant steric disruption caused by the large cylindrical nature of the acetylene bond, in addition to the loss of symmetry introduced by the inclusion of the acetylenic unit.

Table 3. Transition temperatures of unsymmetrical triphenylenes with terminal acetylene units.



Compound	*n*	Transition temperatures (°C)				
		Cr		Col$_h$		I
12	3	●	53.3	●	97.6	●
13	4	●	62.8	●	84.0	●
14	5	●	51.5	●	67.1	●
15	6	●	52.4	●	68.3	●

Table 4. Transition temperatures of unsymmetrical linear alkoxy chain triphenylenes based on HAT6 (*9*).



Compound	*R*	Transition temperatures (°C)				
		Cr		Col$_h$		I
16	$-C_2H_5$	●	57.3	●	79.1	●
17	$-C_3H_7$	●	60.6	●	84.8	●
18	$-C_4H_9$	●	59.7	●	95.1	●
19	$-C_5H_{11}$	●	57.7	●	94.5	●
2	$-C_6H_{13}$	●	67.6	●	100.1	●
20	$-C_7H_{15}$	●	58.0	●	94.7	●
21	$-C_8H_{17}$	●	52.0	●	86.0	●
22	$-C_{10}H_{21}$	●	45.4	●	59.0	●

Whilst the melting points of compounds **12**–**15** may follow the same trend as their alkoxy counterparts (**19**–**21** and **2**), however it is clear from Table 3 that other factors are at work with respect to the columnar phase stabilities. It might be expected that compound **13** should generate the most stable columnar mesophase since it possesses a carbon chain length similar to that of the otherwise symmetrical material as illustrated by the simple model shown in Figure 2. However, compound **12** shows a much higher Col$_h$ (Figure 3) stability, which can be explained by considering the cone of rotation of the acetylenic bond which is important to the columnar phase stability. The rigid linear *sp* acetylenic unit can rotate to cause much disruption to the columnar packing of the molecules. Hence, as can be observed in Figure 2, since the acetylenic unit essentially points

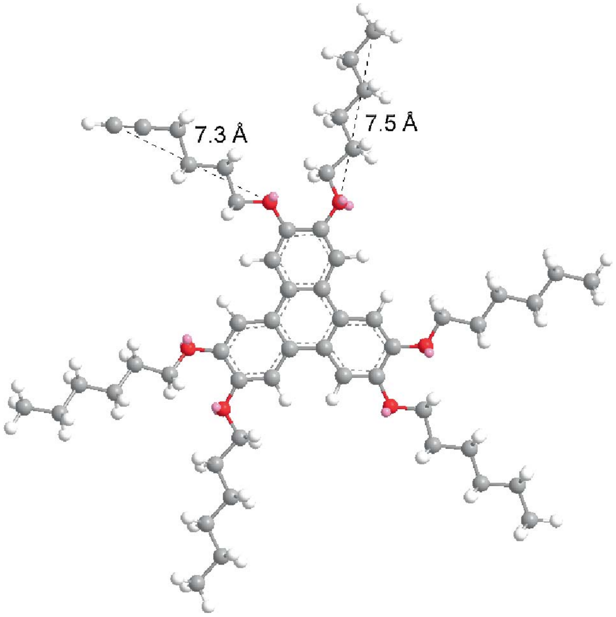


Figure 2. Simple model of compound **13**, indicating alkoxy chain lengths.

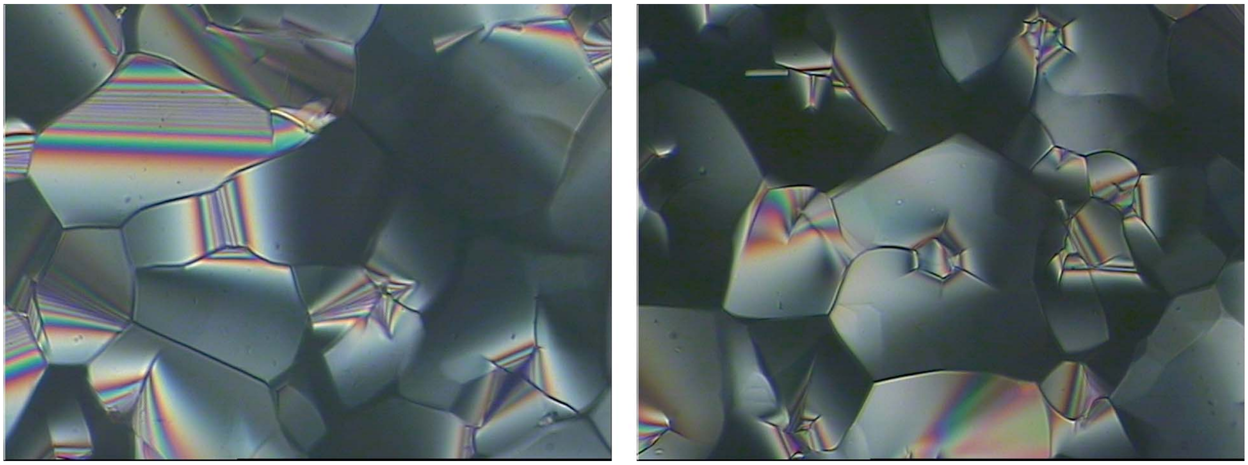
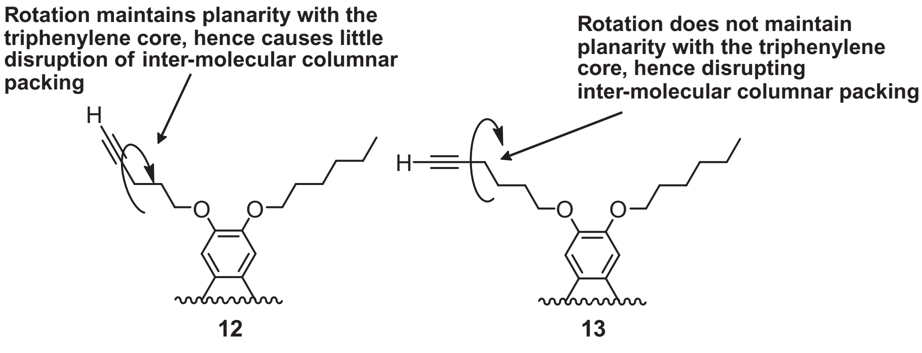


Figure 3. Typical POM textures of Col_h mesophase observed for triphenylenes with a terminal acetylene in a peripheral chain.

outside of the central plane of the triphenylene core (in compound **13**), the cone of rotation of the bond (Figure 4) will be larger than if the acetylenic bond were within the plane of the molecule, as it would be when the carbon chain length count were odd (e.g. compound **12**) as opposed to even (e.g. compound **13**). The cone of rotation of the acetylene-containing chain explains why compound **13** has a lower $T_{Col\text{-}I}$ value than compound **12**; however, it also explains why the $T_{Col\text{-}I}$ value of compound **12** is higher than the comparable compound **19**. In the case of sp^3 hybridised carbons, as in compound **19**, the terminal bond of alkoxy chains with odd numbered carbon units will be outside the cone of rotation just as the even numbered chains are in the case of the *sp* hybridised terminal acetylenes, thus compound **19** possesses a lower $T_{Col\text{-}I}$ value than the analogous compound **12**.

The explanation regarding the cone of rotation, however, does not account for the significantly lowered columnar phase stability of compound **14**, relative to compound **13** and the similarity of the phase stabilities of compounds **14** and **15**. Perhaps a better explanation of the behaviour of these compounds is based on the enhanced rigidity of the acetylenic unit (mentioned previously), coupled with the space filling and steric effect of the acetylenic unit. The large acetylenic unit is capable of filling space around the periphery of the molecule can enhance the columnar phase stability. At the same time as the space-filling effect is enhancing the clearing point, the steric influence of the acetylenic unit impedes columnar packing which destabilises the columnar phase stability and, as has been shown previously, there is a balance between these two influences, which ultimately determines the columnar phase stabilities. Thus, for these acetylene containing compounds with short chain lengths (such as compound **12**) the enhanced attractions caused by the increased rigidity and space-filling effect of the acetylene unit dominate over the disruptive steric effect and offer an enhancement or maintenance of the columnar phase stability. Increasing the length of the alkynyloxy chains (compounds **13** and **14**) increases the flexibility of the chains, destroying the control and balance between the space-filling and



Rotation maintains planarity with the triphenylene core, hence causes little disruption of inter-molecular columnar packing

Rotation does not maintain planarity with the triphenylene core, hence disrupting inter-molecular columnar packing

12

Cr 53.2 Col_h 97.6 I

13

Cr 64.2 Col_h 84.2 I

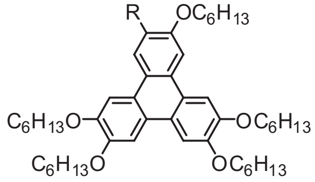
Figure 4. Cone of rotation of terminal acetylenes.

steric effects. Thus, once the alkynyloxy chain length surpass this point of disruption there is little further significant flexibility caused by increasing the chain length, which means that the steric effect of the acetylenic unit is reduced as much as possible and the space-filling effect again becomes the dominant factor, hence offering a slight increase in columnar phase stability of compound **15** relative to compound **14**.

Perhaps the most striking aspect revealed by Table 5 is that all of the acetylene-containing compounds (**23**–**26**) not only exhibit the columnar mesophase (see Figure 5), but the phase stability is significantly enhanced way beyond that of the hexaalkoxy analogues (see Table 4).

Comparing compound **23** with its hexaalkoxy counterpart, compound **18** (Cr 59.7 Col$_h$ 95.1 I), and similarly compound **24** with its hexaalkoxy counterpart, compound **19** (Cr 57.7 Col$_h$ 94.5 I), reveals a difference in columnar phase stabilities of approximately 40°C. This significant enhancement is due primarily to the increased π–π interactions which arise from the inclusion of the acetylenic unit which is more polarisable than the oxygen which it replaces and possesses significant electron density which enhances π–π interactions between triphenylene cores. It is this effect which significantly enhances the columnar phase stabilities of these compounds since it is known that polarisable groups are required to generate a stable columnar structure, and the more polarisable the unit, the more it will conjugate with the triphenylene core, and thus the more stable the columnar mesophase (*15*, *17*). This assertion is further backed up by evidence from our previous work on branched alkoxy chains which revealed only small increases in the columnar phase stabilities (approximately 5°C), due to the space-filling effect being balanced by the steric effect, and hence only small increases in columnar phase stabilities can be achieved.

Table 5. Transition temperatures of unsymmetrical triphenylenes containing acetylenic units.



		Transition temperatures (°C)				
Compound	*R*	Cr		Col$_h$		I
23	$CH_3CH_2CH_2{-}{\equiv}{-}$	•	49.2	•	134.1	•
24	$CH_3CH_2CH_2CH_2{-}{\equiv}{-}$	•	51.9	•	134.2	•
25	$CH_3CH_2CH_2CH_2CH_2{-}{\equiv}{-}$	•	48.1	•	125.5	•
26	$CH_3CH_2CH_2CH_2CH_2CH_2{-}{\equiv}{-}$	•	39.3	•	108.3	•

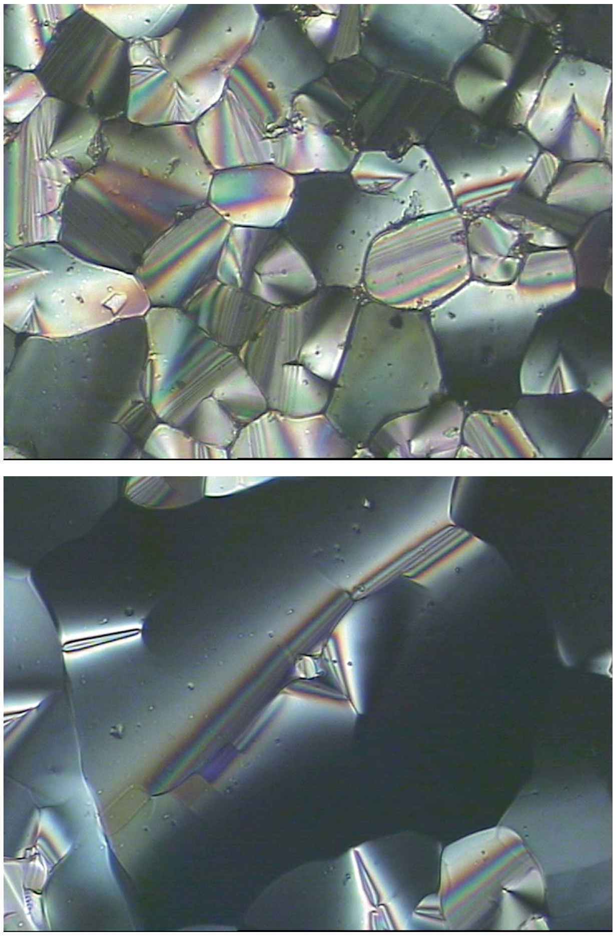


Figure 5. Typical POM textures of the Col$_h$ phase exhibited by compounds **23**–**26**.

The melting points of compounds **23**–**26** (Table 5) are significantly reduced relative to the parent compound **2** and their hexaalkoxy counterparts. There are several factors for this reduction in the melting points of these materials, including the reduction in symmetry and, most significantly in the cases of compounds **23**–**26**, the steric effect of the acetylenic unit. Since the acetylenic unit is next to the triphenylene core in compounds **23**–**26** the disruption to the melting temperature is maximised, and hence the melting points of the materials are 10–20°C lower than the comparable hexaalkoxy systems (see Figure 6 and Table 5).

As can be observed from Table 5 and Figure 6, the trend in melting point closely mirrors the trend in clearing temperatures of compounds **23**–**26** (see Figure 7), and shows that the compound with the highest melting point and columnar mesophase stability is compound **24** which, like the symmetrical HAT6 (**2**), contains six carbons in all of the peripheral units.

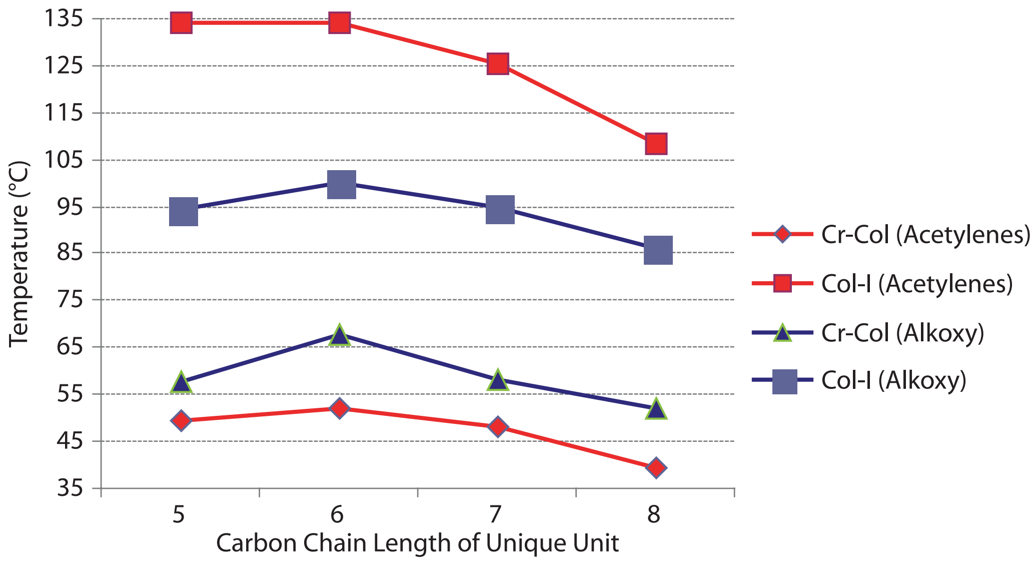


Figure 6. Comparison of transition temperatures of triphenylenes containing acetylenes (**23**–**26**) with triphenylenes containing six alkoxy chains (**19**–**21** and **2**).

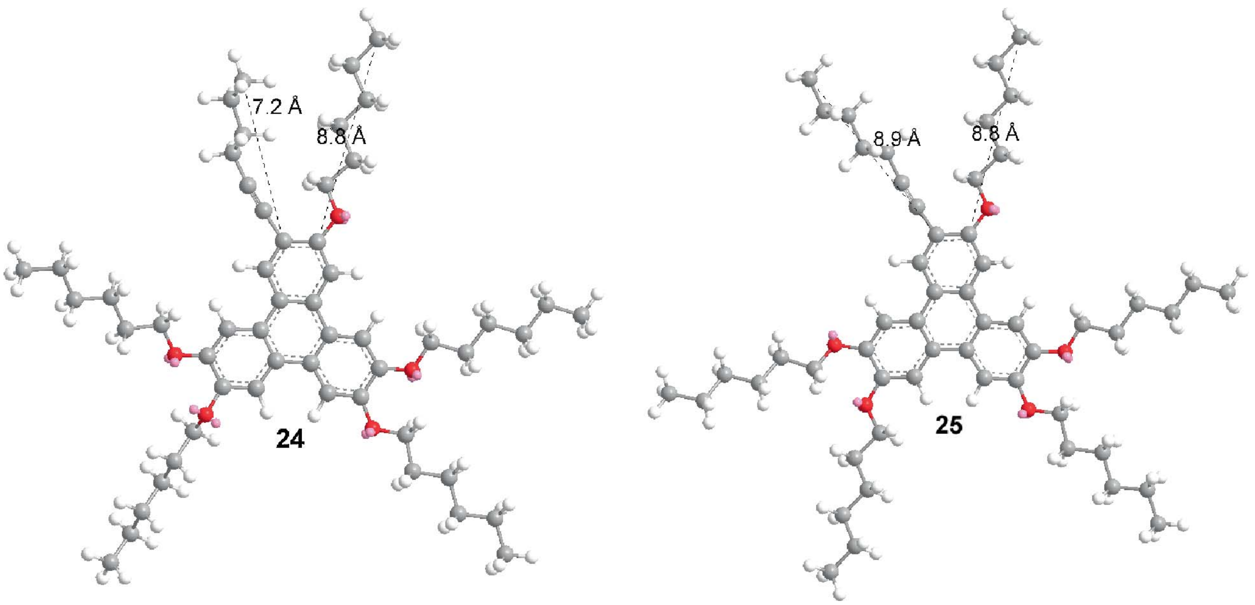


Figure 7. Simple model of compounds **24** and **25**, indicating chain lengths.

When compared with the unsymmetrical triphenylenes containing six linear alkoxy chains, these acetylene-containing compounds behave in a similar fashion, with the transition temperatures increasing up to the entirely six carbon chain length, then decreasing rapidly when the chain length exceeds six carbons as is shown in Figure 6. This result is interesting since, as can be observed in Figure 7, it is compound **25**, not compound **24**, in which the acetylene-containing chain possesses a chain length which is similar to that of the hexyloxy chain, thus it may have been expected that compound **25** would exhibit the highest melting and isotropisation temperatures. Thus, it is not the effect of the acetylene-containing chain length on the overall area of the disc that is the significant factor in this case, but rather the rigidity of the acetylene-containing chain. Thus, as the rigidity of the chain decreases (due to increasing chain length) the isotropisation temperatures decrease rapidly from compounds **24**–**26**.

As this manuscript went to press a paper of some relevance was published detailing complementary research of alkynyl-substituted triphenylenes (*18*).

3. Experimental details

The synthesis of: 2,3,6,7,10,11-hexahydroxytriphenylene (**27**), 2,3,6,7,10-pentahexyloxy-11-hydroxytriphenylene (**34**), HAT6 (**2**) and compounds **26**–**22** have all been reported previously (*9*).

Nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM-Eclipse 400 spectrometer, and all spectra are recorded relative to tetramethylsilane, which was used as an internal standard. Melting points and transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope, and liquid crystal transition temperatures were confirmed by differential scanning calorimetry (Mettler DSC822e). Elemental analysis was performed using a Fisons EA 1108 CHN analyser, and all results obtained were within ±0.30 % of the expected value. The purity of final products was analysed by high-performance liquid chromatography (HPLC) using a Gilson 233XL autosampler, 321 binary solvent pump, Hewlett Packard 1100 series Diode Array Detector, and a Phenomenex Luna 5μm C18(2) column.

2,3,6,7,10,11-Hexapent-4-ynyloxytriphenylene (8)

A stirred mixture of compound **27** (0.50 g, 1.54 mmol), 5-chloropent-1-yne (1.42 g, 0.0139 mol), potassium carbonate (1.90 g, 0.0138 mol), potassium iodide (2.29 g, 0.0138 mol) and butanone (120 ml) was heated under reflux for 9 days. The mixture was cooled to room temperature, filtered to remove the potassium carbonate, extracted into diethyl ether washed with water (twice). The aqueous components were backwashed with diethyl ether, the combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane (DCM) and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a colourless solid.

Yield: 0.23 g (21 %), ^{1}H NMR ($CDCl_3$) δ: 2.03 (6H, t), 2.16 (12H, quint), 2.54 (12H, dt), 4.35 (12H, t), 7.87 (6H, s), ^{13}C NMR ($CDCl_3$) δ: 15.29, 28.36, 67.99, 68.99, 83.65, 107.67, 123.80, 148.82, MS *m/z*: 721 (M^++1), elemental analysis for $C_{48}H_{46}O_6$ requires 79.97 % C, 6.71 % H; found 79.87 % C, 7.00 % H, transition temperatures (°C): Cr 130.2 I.

2,3,6,7,10,11-Hexahex-5-ynyloxytriphenylene (9)

The same procedure was carried out as for compound **8** using the following quantities: compound **27** (0.50 g, 1.54 mmol), 6-chlorohex-1-yne (1.62 g, 0.0139 mol), potassium carbonate (1.90 g, 0.0138 mol), potassium iodide (2.29 g, 0.0138 mol) and butanone (120 ml). The crude product was purified by column chromatography (silica gel, 4:1 hexane/DCM and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a colourless solid.

Yield: 0.80 g (66 %), ^{1}H NMR ($CDCl_3$) δ: 1.85 (12H, quint), 1.99 (6H, t), 2.07 (12H, quint), 2.37 (12H, dt), 4.27 (12H, t), 7.82 (6H, s), ^{13}C NMR ($CDCl_3$) δ: 18.26, 25.29, 28.42, 68.65, 68.99, 84.26, 107.18, 123.62, 148.85, MS *m/z*: 805 (M^+), elemental analysis for $C_{54}H_{60}O_6$ requires 80.56 % C, 7.51 % H; found 80.45 % C, 7.78 % H, transition temperatures (°C): Cr 120.9 I.

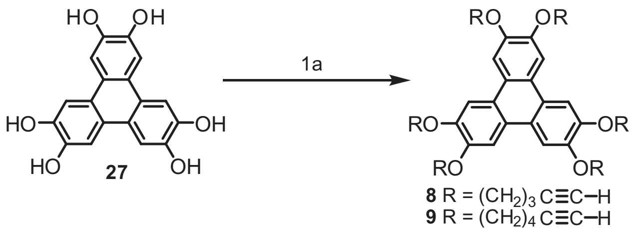
7-Chlorohept-1-yne (32)

1-Bromo-5-chloropentane (**28**, 10.00g, 0.0539 mol) was added dropwise to a stirred, cooled (0°C) mixture of lithiumacetylide ethylene diamine complex (6.12 g, 0.0665 mol) and anhydrous dimethyl sulfoxide (DMSO; 150 ml). The mixture was stirred for 1 hour (gas chromatography (GC) revealed a complete reaction), then water (100 ml) was added cautiously to quench the reaction. The mixture was then extracted into pentane, washed with water (twice) and the aqueous components were back extracted with pentane (twice), the combined organic extracts were dried ($MgSO_4$) and the solvent was carefully distilled off to yield a colourless oil.

Yield: 6.60 g (94 %), ^{1}H NMR ($CDCl_3$) δ: 1.53–1.58 (4H, m), 1.76–1.82 (2H, m), 1.96 (1H, t), 2.21 (2H, dt), 3.54 (2H, t), MS *m/z*: 130 (M^+), 133 (M^++1).

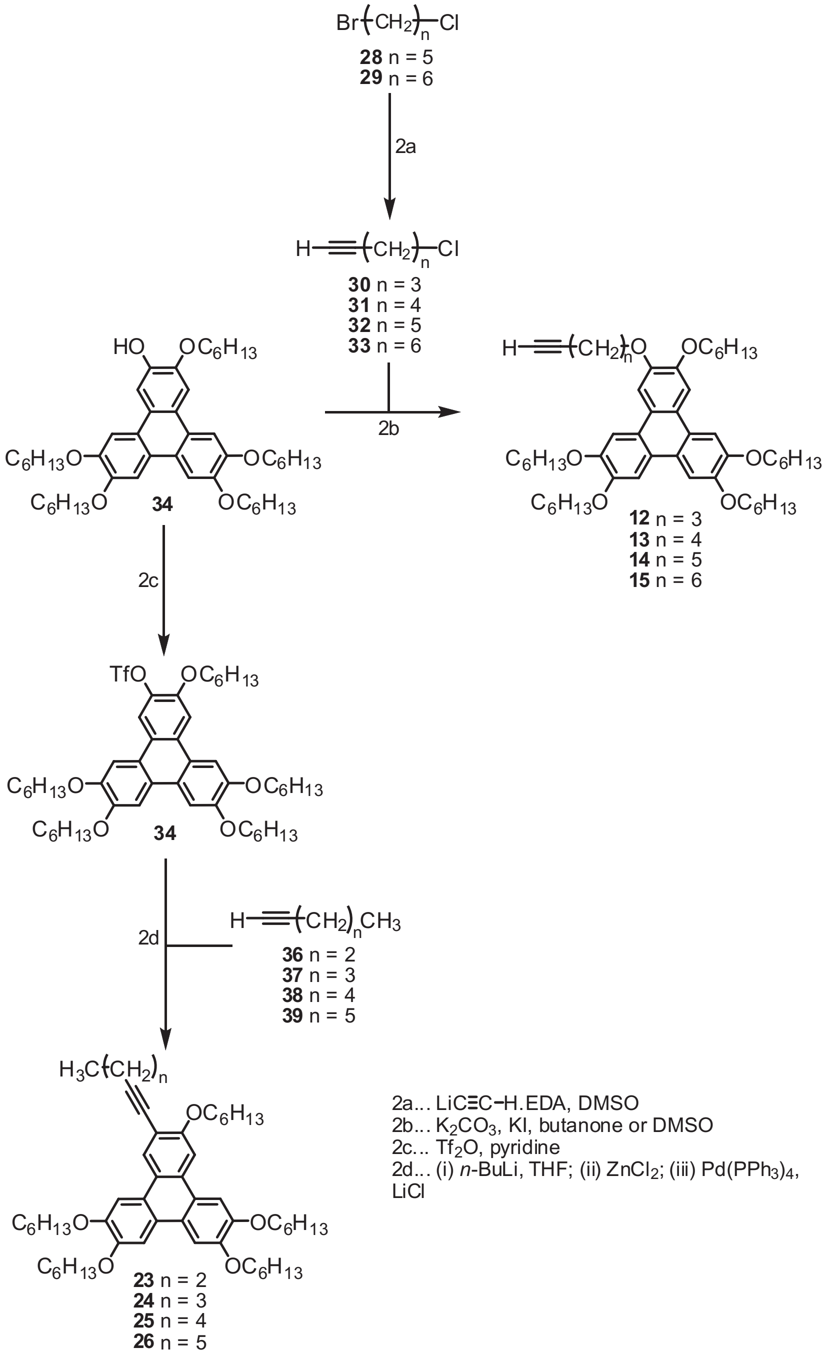
8-Chlorooct-1-yne (33)

1-Bromo-6-chlorohexane (**29**, 5.00 g, 0.0251 mol) was added dropwise to a stirred, cooled (0°C) mixture of lithiumacetylide ethylene diamine complex (2.88 g, 0.0313 mol) and anhydrous DMSO (150 ml). The mixture was stirred for 1 hour (GC revealed a complete reaction), and then water (100 ml) was added cautiously to quench the reaction. The mixture was then extracted into pentane, washed with water (twice) and the aqueous components were back extracted with pentane (twice), the combined organic extracts were dried ($MgSO_4$) and the solvent was carefully distilled off *in vacuo* to yield a colourless oil.



8 R = $(CH_2)_3C{\equiv}C{-}H$
9 R = $(CH_2)_4C{\equiv}C{-}H$

1a... RCl, K_2CO_3, KI, butanone



28 n = 5
29 n = 6

30 n = 3
31 n = 4
32 n = 5
33 n = 6

12 n = 3
13 n = 4
14 n = 5
15 n = 6

36 n = 2
37 n = 3
38 n = 4
39 n = 5

23 n = 2
24 n = 3
25 n = 4
26 n = 5

2a... $LiC{\equiv}C{-}H$.EDA, DMSO
2b... K_2CO_3, KI, butanone or DMSO
2c... Tf_2O, pyridine
2d... (i) *n*-BuLi, THF; (ii) $ZnCl_2$; (iii) $Pd(PPh_3)_4$, LiCl

Yield: 3.26 g (90 %), ^{1}H NMR (CDCl$_3$) δ: 1.41–1.46 (4H, m), 1.54 (2H, quint), 1.78 (2H, quint), 1.94 (1H, t), 2.19 (2H, dt), 3.53 (2H, t), MS m/z: 146 (M$^+$), 144 (M$^+$).

2,3,6,7,10-Pentahexyloxy-11-pent-4-ynyloxytriphenylene (12)

A stirred mixture of compound **34** (0.50 g, 0.672 mmol), 5-chloropent-1-yne (**30**, 0.30 g, 2.68 mmol), potassium carbonate (0.46 g, 3.35 mmol), and potassium iodide (0.20 g, 120 mmol) in butanone (120 ml) was heated under reflux for 7 days (thin layer chromatography (TLC) revealed a complete reaction). The mixture was cooled to room temperature, filtered to remove the potassium carbonate and the solvent was removed *in vacuo*. The product was extracted into diethyl ether, washed with water, the aqueous component was back extracted with diethyl ether and the combined ethereal extracts were dried (MgSO$_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 1:1 hexane/DCM and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P$_2$O$_5$) to yield a colourless waxy solid.

Yield: 0.32 g (59 %), ^{1}H NMR (CDCl$_3$) δ: 0.93 (15H, t), 1.34–1.41 (18H, m), 1.58 (10H, quint), 1.85 (2H, quint), 1.94 (10H, quint), 1.98 (1H, t), 2.07 (2H, quint), 2.36 (2H, dt), 4.23 (10H, 5×t), 4.26 (2H, t), 7.84 (6H, s), ^{13}C NMR (CDCl$_3$) δ: 14.05, 18.07, 18.25, 22.65, 25.27, 25.84, 31.68, 69.59, 69.05, 69.59, 69.71, 107.13, 107.31, 107.32, 107.37, 107.38, 12352, 123.54, 123.56, 123.58, 123.64, 123.73, 148.74, 148.95, 148.99, 149.01, MS m/z: 810 (M$^+$), elemental analysis for C$_{53}$H$_{78}$O$_6$ requires 78.47 % C, 9.69 % H; found 78.70 % C, 9.90 % H, transition temperatures (°C): Cr 53.3 Col$_h$ 97.6 I.

2,3,6,7,10-Pentahexyloxy-11-hex-5-ynyloxytriphenylene (13)

The same procedure was carried out as for compound **12** using the following quantities: compound **34** (0.50 g, 0.672 mmol), 6-chlorohex-1-yne (**31**, 0.30 g, 2.59 mmol), potassium carbonate (0.46 g, 3.35 mmol), and potassium iodide (0.20 g, 120 mmol) in butanone (120 ml). The crude product was purified by column chromatography (silica gel, 1:1 hexane/DCM, and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P$_2$O$_5$) to yield a colourless waxy solid.

Yield: 0.33 g (60 %), ^{1}H NMR (CDCl$_3$) δ: 0.94 (15H, t), 1.31–1.48 (22H, m), 1.57 (10H, quint), 1.94 (10H, quint), 2.01 (1H, t), 2.15 (2H, quint), 2.53 (2H, dt), 4.22 (10H, 2×t), 4.34 (2H, t), 7.83 (5H, s), 7.86 (1H, s), ^{13}C NMR (CDCl$_3$) δ: 14.05, 15.28, 22.65, 25.85, 28.44, 29.39, 29.41, 31.66, 31.68, 68.03, 68.80, 69.61, 69.68, 69.69, 69.74, 107.20, 107.29, 107.34, 107.37, 107.73, 123.52, 123.54, 123.61, 123.68, 123.87, 148.63, 148.96, 148.96, 148.98, 149.00, 149.05, MS m/z: 825 (M$^+$), elemental analysis for C$_{54}$H$_{80}$O$_6$ requires 78.60 % C, 9.77 % H; found 78.48 % C, 9.87 % H, transition temperatures (°C): Cr 62.8 Col$_h$ 84.0 I.

2-Hept-6-ynyloxy-3,6,7,10,11-pentahexyloxytriphenylene (14)

The same procedure was carried out as for compound **12** using the following quantities: compound **34** (0.50 g, 0.672 mmol), compound **32** (0.26 g, 1.99 mmol), potassium carbonate (0.28 g, 2.03 mmol) and potassium iodide (0.20 g, 120 mmol) in DMSO (100 ml). The crude product was purified by column chromatography (silica gel, 4:1 hexane/DCM and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1), and dried (P$_2$O$_5$) to yield a colourless solid.

Yield: 0.12 g (21 %), ^{1}H NMR (CDCl$_3$) δ: 0.93 (15H, t), 1.35–1.45 (20H, m), 1.58 (10H, quintet), 1.64 (4H, 2×quint), 1.94 (12H, quint), 1.96 (1H, t), 2.27 (2H, dt), 4.22 (10H, t), 4.24 (2H, t), 7.83 (6H, s), ^{13}C NMR (CDCl$_3$) δ: 14.06, 18.43, 22.67, 25.42, 25.86, 28.33, 28.99, 29.43, 29.72, 31.69, 68.36, 69.49, 69.66, 69.72, 69.74, 107.26, 107.36, 107.39, 107.44, 123.58, 123.62, 123.65, 123.71, 148.85, 148.96, 148.98, 149.00, MS m/z: 839 (M$^+$+1), elemental analysis for C$_{55}$H$_{82}$O$_6$ requires 78.71 % C, 9.85 % H; found 78.58 % C, 10.04 % H, transition temperatures (°C): Cr 51.5 Col$_h$ 67.1 I.

2,3,6,7,10-Pentahexyloxy-11-oct-7-ynyloxytriphenylene (15)

The same procedure was carried out as for compound **12** using the following quantities: compound **34** (0.50 g, 0.672 mmol), compound **33** (0.30 g, 2.08 mmol), potassium carbonate (0.28 g, 2.03 mmol) and potassium iodide (0.20 g, 120 mmol) in DMSO (100 ml). The crude product was purified by column chromatography (silica gel, 4:1 hexane/DCM and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1), and dried (P$_2$O$_5$) to yield a colourless solid.

Yield: 0.31 g (54 %), ^{1}H NMR (CDCl$_3$) δ: 0.93 (15H, 5×t), 1.35–1.45 (22H, m), 1.51–1.63 (14H, m), 1.94 (12H, quint), 1.95 (1H, t), 2.22 (2H, dt), 4.23 (12H, t), 7.83 (6H, t), ^{13}C NMR (CDCl$_3$) δ: 14.05, 18.35, 22.66, 25.69, 25.85, 28.43, 28.55, 29.35, 29.42, 31.68, 68.22, 69.55, 69.66, 69.70, 69.73, 107.34, 107.35, 107.39, 123.54, 123.58, 123.62, 148.89, 148.97, 148.99, MS *m/z*: 853 (M^++1), elemental analysis for $C_{56}H_{84}O_6$ requires 78.83 % C, 9.92 % H; found 78.59 % C, 9.69 % H, transition temperatures (°C): Cr 52.4 Col$_h$ 68.3 I.

2-Trifluoromethylsulfonato-3,6,7,10,11-pentahexyloxytriphenylene (35)

Triflic anhydride (3.75 g, 0.133 mol) was added dropwise to a stirred, cooled (0°C) mixture of compound **34** (8.10 g, 0.109 mol) in anhydrous pyridine (200 ml) under an atmosphere of dry nitrogen. The mixture was slowly warmed to room temperature (overnight) then poured into water. The mixture was extracted into diethyl ether and washed with 10% hydrochloric acid solution, water and brine, the aqueous components were backwashed with further portions of diethyl ether, the combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane with increasing volume fractions of DCM) to yield a dark blue waxy solid.

Yield: 7.04 g (74 %), ^{1}H NMR ($CDCl_3$) δ: 0.94 (15H, 5×t), 1.32-1.46 (20H, m), 1.54–1.60 (10H, m), 1.95 (10H, 5×quint), 4.23 (8H, 4×t), 4.28 (2H, t), 7.73 (1H, s), 7.81 (2H, 2×s), 7.90 (1H, s), 8.21 (1H, s), ^{13}C NMR ($CDCl_3$) δ: 14.06, 22.67, 25.86, 28.96, 29.12, 29.43, 29.48, 31.69, 67.71, 107.34, 123.61, 148.97, ^{19}F NMR ($CDCl_3$) δ: –73.53, MS *m/z*: 877 (M^++1), transition temperatures (°C): Col$_h$ 168.0 I.

2,3,6,7,10-Pentahexyloxy-11-pent-1-ynyltriphenylene (23)

A solution of *n*-butyllithium (1.4 ml, 2.5 M in hexanes, 3.5 mmol) was added dropwise to a stirred, cooled (0°C) mixture of pent-1-yne (**36**, 1.00 g, 0.0147 mol) in anhydrous tetrahydrofuran (THF; 100 ml) under an atmosphere of dry nitrogen and stirred together for 1 hour. Zinc(II) chloride (0.53 g, 3.90 mmol) was dissolved in anhydrous THF (100 ml) and added to the mixture, which was slowly warmed to room temperature. The mixture was stirred together for 1 hour and tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.0607 mmol), lithium chloride (0.05 g, 4.76 mmol) and compound **35** (1.00 g, 1.14 mmol) in anhydrous THF (50 ml) were added and the mixture was heated under reflux for 16 hours. The mixture was cooled to room temperature, the product was extracted into diethyl ether and washed with water (twice), the aqueous components were backwashed with diethyl ether and the combined organic components were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane with increasing volume fractions of DCM, and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a yellow solid.

Yield: 0.28 g (31 %), ^{1}H NMR ($CDCl_3$) δ: 0.92–0.96 (15H, m), 1.14 (3H, t), 1.36–1.62 (20H, m), 1.57 (10H, quint), 1.73 (2H, sext), 1.89–1.98 (10H, m), 2.54 (2H, t), 4.23 (10H, 5×t), 7.75 (1H, s), 7.80 (1H, s), 7.81 (1H, s), 7.86 (1H, s), 7.88 (1H, s), 8.46 (1H, s), ^{13}C NMR ($CDCl_3$) δ: 13.65, 14.06, 17.86, 21.89, 22.36, 22.67, 25.84, 25.87, 29.35, 29.37, 29.38, 29.43, 31.70, 31.72, 69.09, 69.28, 69.52, 69.85, 69.88, 94.62, 104.61, 106.42, 107.43, 107.95, 113.27, 122.71, 122.96, 123.02, 123.50, 125.09, 128.19, 129.65, 148.81, 149.37, 149.95, 153.81, 157.69, MS *m/z*: 794 (M^+), elemental analysis for $C_{53}H_{78}O_5$ requires 80.05 % C, 9.89 % H; found 80.13 % C, 9.70 % H, transition temperatures (°C): Cr 49.2 Col$_h$ 134.1 I.

2,3,6,7,10-Pentahexyloxy-11-hex-1-ynyltriphenylene (24)

The same procedure was carried out as detailed for compound **23** using the following quantities: *n*-butyllithium (1.4 ml, 2.5 M in hexanes, 3.5 mmol), hex-1-yne (compound **37**, 1.00 g, 0.0122 mol), zinc(II) chloride (0.53 g, 3.90 mmol) tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.0607 mmol), lithium chloride (0.05 g, 4.76 mmol), compound **35** (1.00 g, 1.14 mmol) and THF (250 ml). The crude product was purified by column chromatography (silica gel, hexane with increasing volume fractions of DCM, and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a colourless solid.

Yield: 0.09 g (10 %), ^{1}H NMR ($CDCl_3$) δ: 0.92-0.96 (15H, m), 0.99 (3H, t), 1.32–1.44 (20H, m), 1.53–1.61 (4H, m), 1.68 (2H, sext), 1.91–1.98 (10H, m), 2.56 (2H, t), 4.23 (10H, 5×t), 7.75 (1H, s), 7.80 (1H, s), 7.81 (1H, s), 7.86 (1H, s), 7.88 (1H, s), 8.46 (1H, s), ^{13}C NMR ($CDCl_3$) δ: 13.72, 14.06, 19.60, 22.08, 22.67, 22.69, 25.84, 25.87, 29.35, 29.37, 29.38, 29.43, 29.71, 30.99, 31.72, 69.09, 69.28, 69.53, 69.85, 69.84, 94.77, 104.61, 106.43, 106.94, 107.42, 107.96, 113.28, 121.82, 122.71, 122.96, 123.02, 123.38, 123.50, 128.18, 129.65, 148.75, 149.37, 149.95, 157.69, MS *m/z*: 809 (M^++1), elemental analysis for $C_{54}H_{80}O_5$ requires 80.15 % C, 9.96 % H; found 80.01 % C, 9.85 % H, transition temperatures (°C): Cr 51.9 Col$_h$ 134.2 I.

2-Hept-1-ynyl-3,6,7,10,11-pentahexyloxytriphenylene (25)

The same procedure was carried out as detailed for compound **23** using the following quantities: *n*-

butyllithium (1.4 ml, 2.5 M in hexanes, 3.5 mmol), hept-1-yne (compound **38**, 1.00 g, 0.0104 mol), zinc(II) chloride (0.53 g, 3.90 mmol) tetrakis(triphenylphosphine)-palladium(0) (0.07 g, 0.0607 mmol), lithium chloride (0.05 g, 4.76 mmol), compound **35** (1.00 g, 1.14 mmol) and THF (200 ml). The crude product was purified by column chromatography (silica gel, hexane with increasing volume fractions of DCM, and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a colourless solid.

Yield: 0.55 g (59 %), ^{1}H NMR ($CDCl_3$) δ: 0.93 (15H, 3×t), 0.95 (3H, t), 1.32–1.46 (20H, m), 1.49–1.65 (14H, m), 1.70 (2H, sext), 1.89-1.99 (10H, m), 2.55 (2H, t), 4.23 (10H, 4×t), 7.75 (1H, s), 7.80 (1H, s), 7.81 (1H, s), 7.86 (1H, s), 7.88 (1H, s), 8.46 (1H, s), ^{13}C NMR ($CDCl_3$) δ: 14.00, 19.85, 22.28, 22.62, 22.64, 25.81, 28.61, 29.33, 29.40, 31.17, 31.66, 68.97, 69.13, 69.38, 69.73, 69.76, 94.68, 104.48, 106.22, 106.75, 107.27, 107.79, 113.16, 122.61, 122.85, 122.90, 123.39, 124.98, 128.11, 129.53, 148.69, 149.25, 149.83, 157.56, MS *m/z*: 823 (M^++1), elemental analysis for $C_{55}H_{82}O_5$ requires 80.24 % C, 10.04 % H; found 80.26 % C, 10.17 % H, transition temperatures (°C): Cr 48.1 Col$_h$ 125.5 I.

2,3,6,7,10-Hexyloxy-11-oct-1-ynyltriphenylene (26)

The same procedure was carried out as detailed for compound **23** using the following quantities: *n*-butyllithium (1.4 ml, 2.5 M in hexanes, 3.5 mmol), oct-1-yne (compound **39**, 1.00 g, 9.09 mmol), zinc(II) chloride (0.53 g, 3.90 mmol) tetrakis(triphenylphosphine)-palladium(0) (0.07 g, 0.0607 mmol), lithium chloride (0.05 g, 4.76 mmol), compound **35** (1.00 g, 1.14 mmol) and THF (250 ml). The crude product was purified by column chromatography (silica gel, hexane with increasing volume fractions of DCM, and alumina, hexane with increasing volume fractions of DCM), recrystallised from ethanol/toluene (10:1) and dried (P_2O_5) to yield a colourless solid.

Yield: 0.49 g (51 %), ^{1}H NMR ($CDCl_3$) δ: 0.91–0.96 (18H, m), 1.33–1.45 (24H, m), 1.53–1.61 (12H, m), 1.70 (2H, sext), 1.89–1.98 (10H, m), 2.55 (2H, t), 4.23 (10H, 4×t), 7.75 (1H, s), 7.80 (1H, s), 7.81 (1H, s), 7.86 (1H, s), 7.88 (1H, s), ^{13}C NMR ($CDCl_3$) δ: 14.05, 14.12, 19.92, 22.62, 22.65, 22.68, 25.83, 28.71, 28.90, 29.35, 29.41, 31.48, 31.68, 69.09, 69.22, 69.49, 69.82, 69.86, 94.81, 104.63, 106.34, 106.89, 107.38, 107.90, 113.27, 122.70, 122.93, 122.99, 123.46, 125.06, 128.20, 129.62, 148.78, 149.34, 149.92, 157.63, MS *m/z*: 837 (M^++1), elemental analysis for $C_{56}H_{84}O_5$ requires 80.33 % C, 10.11 % H; found 80.03 % C, 10.05 % H, transition temperatures (°C): Cr 39.3 Col$_h$ 108.3 I.

4. Conclusions

A number of symmetrical and unsymmetrical triphenylene-based materials containing alkynyloxy chains have been prepared. The symmetrical compounds (**8** and **9**) contain six alkynyloxy chains, and exhibit enhanced melting points relative to the comparable hexaalkoxy analogues HAT5 and HAT6. It was noted that the columnar mesophase thermal stability of the compounds was not enhanced to the same degree as the melting point, with only compound **8** exhibiting a columnar mesophase, albeit transiently and monotropically. It is likely that the enhancement of the melting points of the terminal acetylene-containing materials is due to combinations of increased chain rigidity, and increased space filling due to the acetylenic unit, which would not affect the columnar phase stabilities to the same degree as the melting points, as has already been shown.

Unsymmetrical alkynyloxy-containing triphenylene-based materials that have been synthesised all have reduced melting points and isotropisation temperatures relative to their hexaalkoxy counterparts. This reduction in melting and clearing temperatures is due to steric disruption of the acetylenic unit and loss of symmetry within the molecule. A possible odd–even effect was noted at small alkynyloxy chain lengths, where this effect could be more dominant than other factors governing columnar phase stabilities. It is also possible that at short chain lengths the space-filling effect and enhanced rigidity offered by the acetylenic unit enhance (or maintain) columnar phase stability, and that as the alkynyloxy chain length increases the increased flexibility of the chain destroys this control and the steric effect of the acetylenic unit reduces the columnar phase stability. At even longer alkynyloxy chain lengths the increase in flexibility then appears to become less of a factor as the overall increase in flexibility is minimal, thus the steric and space filling effects and increased rigidity and enhanced π–π interactions offered by the acetylenic unit again become more dominant.

A series of acetylene-containing triphenylene-based compounds (**23**–**26**) has been synthesised, all of which exhibit the hexagonal columnar mesophase. Compounds **23**–**26** all possess considerably lower melting points and significantly higher clearing points than that of their hexaalkoxy counterparts or the symmetrical parent compound HAT6 (**2**). This columnar phase enhancement has been demonstrated to be due to combinations of the space filling effect of the acetylenic unit and, more importantly, the enhanced π–π interactions introduced by the acetylenic unit. It has also been noted that the melting and clearing points of these materials do not appear to be influenced by the symmetrical length of the peripheral acetylenic chain to any significant degree. Rather, it appears that the overall rigidity of the molecule, as affected by the peripheral chains, is the most significant factor with regards to columnar phase stabilities and melting points in the case of these acetylene-containing materials. The low melting points and high clearing points of compounds **23–26** are highly significant when compared with the symmetrical compounds HAT6 (**2**) and **5**. They reveal that the unsymmetrical materials benefit from the enhanced interactions afforded by the inclusion of the acetylenic unit (relative to compound **2**) and reduced steric influences than would be present when all six peripheral units contained an acetylenic unit as in compound **5**.

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