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Amide, urea and thiourea-containing triphenylene derivatives: influence of H-bonding on mesomorphic properties

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The synthesis and thermotropic properties are reported for a series of hexaalkoxytriphenylenes that contain an amide, urea or thiourea group in one of their alkoxy tails. The intermolecular hydrogen bonding abilities of these molecules have a disturbing influence on the formation and stability of the columnar liquid crystalline phases. The stronger the hydrogen bonding the more the liquid crystallinity is suppressed, probably due to disturbance of the π–π stacking of the triphenylene discs. As a direct result, urea- and amide-containing triphenylene derivatives are not liquid crystalline, but several thiourea derivatives show hexagonal columnar mesophases.

1. Introduction

Discotic molecules, such as 2,3,6,7,10,11-hexakishexyloxytriphenylene (HAT6) and several of its derivatives [1], self-assemble into columns based on favourable π–π interactions between their polyaromatic cores [2]. This particular type of interaction leads to the formation of a one-dimensional pathway for transport of charge carriers along the columns [3]. Based on their semiconducting properties [4], these π-conjugated materials offer a remarkable potential as active elements in electronic devices such as field-effect transistors (FETs), photovoltaic solar cells and light-emitting diodes (LEDs) [5].

One of the key factors for a good performance of organic-based electronic devices is the efficiency of charge transport through self-assembled columnar stacks of molecules, from one electrode to another [6]. This efficiency is strongly correlated with the degree of ordering in the active organic layer(s), present as a thin crystalline or liquid crystalline film in an electronic device [7]. Since in columnar liquid crystals the disc-like molecules can still oscillate, slide out of the column or rotate around the columnar axis [8], thus disturbing the optimal ordering, restricting or controlling these movements in the columnar phase is strongly desired.

Hydrogen (H)-bonding interactions provide an option to yield such control. These interactions play an important role in the supramolecular chemistry of self-assembled molecules [9], and are considered to be an important tool to construct interesting functional liquid-crystalline assemblies [10].

In columnar liquid crystalline phases, polyaromatic molecules stack on top of each other with an intermolecular π–π stacking distance of about 3.6 Å [11]. In the case of H-bonding enforced discotic mesophases, the π–π stacking distance can be reduced to 3.18 Å [12], which is expected to lead to higher charge mobilities [13]. However, even in this case of very short π–π distances, as obtained for hexaazatriphenylene derivatives [14], a disappointing charge carrier mobility of only $0.08\,cm^2\,V^{-1}\,s^{-1}$ at 200°C was found [12].

A higher charge carrier transport was recently obtained in our labs with a compound containing a C_3-symmetrical 1,3,5-benzenetrisamide central unit surrounded by three pendant triphenylene groups, in which triple H-bonds between the benzenetrisamides are present [15]. In this particular case, successive triphenylene cores in the columnar stacks are rotated as little as 15° with respect to each other. This small rotation of successive triphenylene cores allowed charge carrier mobilities as high as $0.12\,cm^2\,V^{-1}\,s^{-1}$ at 180°C. Theory predicts that a small rotation results in a large splitting of the frontier orbital electronic levels (HOMO, LUMO), which is favourable for a high charge carrier mobility [16].

Amide H-bonds [17] have often been used to decrease the intracolumnar distance and lock the movements of

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the disc-like molecules in the columns, as seen by the work of Meijer and Nuckolls and their co-workers [18]. This results in higher clearing points for the amides than for the corresponding ester derivatives, as observed for a series of symmetrically substituted triphenylenes [19]. Furthermore, intercolumnar H-bonding has been used to stabilize columnar assemblies of carboxylic acid-terminated triphenylene and hexabenzocoronene derivatives, by locking the disc-like molecules into a stable columnar phase [20]. Detailed information about stabilization and mixing behaviour has also been provided for mixtures of H-bond forming triphenylene materials and the non-H-bond forming HAT6 [21].

Since H-bonding interactions provide a promising tool for the stabilization of a columnar organization, a new approach of H-bond stabilization of columnar mesophases is explored in this work. This approach is based on the replacement of one of the six alkoxy substituents of the HAT6 molecule with an alkoxy group containing a urea, amide or thiourea group, capable of H-bonding formation (figure 1). The parent molecule (HAT6) shows a columnar discotic mesophase between approximately 70°C and 100°C [crystal (Cr) 67°C (40 kJ mol^{-1}) Col$_h$ 98°C (5 kJ mol^{-1}) isotropic (I)] [11]. However, the charge carrier mobility, in its liquid crystalline phase, is rather low (2×10^{-3} cm^2 V^{-1} s^{-1}) due to the highly dynamic movements of the HAT6 molecules inside the columns [8]. It could be expected that H-bonding, among the amide, urea or thiourea groups along the columnar axis, stabilizes the columnar phase by diminishing the movements of the triphenylene molecules. In particular, it would reduce the tendency to slide out of the column, rotate around the columnar axis or oscillate inside the column. Therefore, a series of new triphenylene derivatives (**8-nXm**) with hydrogen bond-forming groups in one of their tails was synthesized, and their thermotropic properties were investigated. The structures of the investigated compounds are shown in figure 1.

2. Experimental

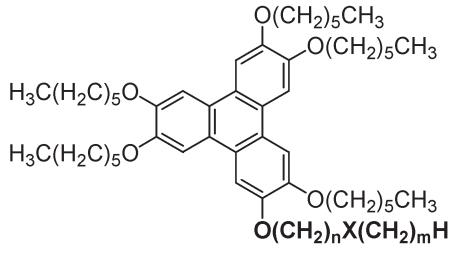
2.1. *Measurements*

^{1}H NMR (300 MHz and 400 MHz) and ^{13}C NMR (75 MHz and 100 MHz) spectra were obtained with Bruker spectrometers, using $CDCl_3$ as a solvent. Melting points, thermal phase transition temperatures and optical investigation of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarizing optical microscope equipped with a Mettler FP82HT hot stage, which was controlled by a Mettler FP80HT central processor.

Differential scanning calorimetry (DSC) thermograms were obtained on a Perkin Elmer DSC-7 system using 2–5 mg samples in 30 µl sample pans and a scan rate of 10°C min^{-1}. Transition enthalpies, ΔH, were calculated in kJ mol^{-1}.

Temperature-dependent X-ray diffractograms were measured on a Philips (Panalytical) X'pert Pro machine equipped with an Anton Paar camera for temperature control. For the measurements in the small angle region, the sample was spread in the isotropic or the liquid crystalline phase on a thin glass slide (about 15 µm thick), which was placed on a temperature regulated flat copper sample stage.

The accurate masses were obtained using a Finnigan MAT 95 mass spectrometer operating in the 70 eV EI mode at a resolution of 5500. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (Maldi-tof MS) mass spectra were obtained on an Ultraflex spectrometer, using 2,5-dihydroxybenzoic acid



8-nXm

8-3T1 (n = 3, X = -NHCSNH-, m = 1)

8-3T2 (n = 3, X = -NHCSNH-, m = 2)

8-4T1 (n = 4, X = -NHCSNH-, m = 1)

8-4T2 (n = 4, X = -NHCSNH-, m = 2)

8-10T2 (n = 10, X = -NHCSNH-, m = 2)

8-4A2 (n = 4, X = -NHCO-, m = 2)

8-10A7 (n = 10, X = -NHCO-, m = 7)

8-4U2 (n = 4, X = -NHCONH-, m = 2)

8-6U6 (n = 6, X = -NHCONH-, m = 6)

8-10U6 (n = 10, X = -NHCONH-, m = 6)

Figure 1. Structures of the triphenylene derivatives, **8-nXm**, (X: T=thiourea; U=urea; A=amide).

(DHB; Sigma-Aldrich) as a matrix. Infrared spectra (FTIR) were obtained using a Bruker Vector 22 spectrometer.

2.2. *Synthesis*

All solvents were PA quality. All reactions were carried out under a nitrogen or argon atmosphere, if required. Dry dichloromethane was freshly distilled from anhydrous calcium hydride. All starting materials were obtained from Sigma-Aldrich and used as received.

2.2.1. 1-(4-Bromobutoxy)-2-hexyloxybenzene, 2–4. A stirred mixture of 2-hexyloxyphenol **1** (7.70 g, 0.04 mol) [22], 1,4-dibromobutane (25.7 g, 0.12 mol) and potassium carbonate (20.0 g) in butanone (100 ml) was refluxed for 8 h under nitrogen. After evaporating about half the solvent from the reaction mixture, 150 ml water was added and the product was extracted with 3×50 ml dichloromethane. The organic layers were dried over anhydrous sodium sulfate, evaporated and the crude product was purified by column chromatography on silica gel with light petroleum–dichloromethane (2:1) as eluent, to obtain **2–4** as pale yellow oil (11.9 g, 91%). ^{1}H NMR: δ 6.91 (4H, s, ArH), 4.06–3.97 (4H, dt, J=6.1 Hz, OCH_2), 3.54 (2H, t, J=6.0 Hz, CH_2Br), 2.15–1.38 (12H, m, CH_2), 0.95 (3H, t, J=5.6 Hz, CH_3). ^{13}C NMR: δ 149.35, 148.83 (1,2-ArC–O), 121.41 (6-ArC–H), 120.90 (3-ArC–H), 114.24 (5-ArC–H), 113.70 (4-ArC–H), 69.00, 68.31 (OCH_2), 33.67 (CH_2Br), 31.67–22.71 (CH_2), 14.13 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{16}H_{25}BrO_2$, 328.1038; found, 328.1038.

The other compounds **2-n** were prepared similarly.

2.2.2. 1-(4-Azidobutoxy)-2-hexyloxybenzene, 3–4. A stirred mixture of 1-(4-bromobutoxy)-2-hexyloxybenzene **2–4** (4.98 g, 15.0 mmol) and sodium azide (2.95 g, 45.0 mmol) in ethanol (50 ml) was refluxed for 8 h. After partial evaporation of the solvent, the reaction mixture was poured into water (150 ml) and the product was extracted with 2×50 ml of dichloromethane. The organic layer was then dried on anhydrous sodium sulfate and the solvent was evaporated under vacuum. 1-(4-Azidobutoxy)-2-hexyloxybenzene **3–4** (2.55 g, 56%) was obtained as pale yellow oil, after purification on a silica gel column with light petroleum–dichloromethane (2:1) as eluent. ^{1}H NMR: δ 6.90 (4H, s, ArH), 4.06–3.96 (4H, dt, J=5.8 Hz, OCH_2), 3.39 (2H, t, J=6.3 Hz, CH_2N_3), 1.94–1.31 (12H, m, CH_2), 0.92 (3H, t, J=6.6 Hz, CH_3). ^{13}C NMR: δ 149.32 (1-ArC–O), 148.79 (2-ArC–O), 121.40 (6-ArC–H), 120.88 (3-ArC–H), 114.24 (5-ArC–H), 113.72 (4-ArC–H), 69.02, 68.58 (OCH_2), 51.26 (CH_2N_3), 31.61–22.65 (CH_2), 14.05 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{16}H_{25}N_3O_2$, 291.1947; found, 291.1949.

The other compounds **3-n** were prepared similarly.

2.2.3. 4-(2-Hexyloxyphenoxy)butylamine, 4–4. A mixture of 1-(4-azidobutoxy)-2-hexyloxybenzene **3–4** (5.41 g, 18.0 mmol) and $LiAlH_4$ (0.36 g, 94.0 mmol) in dry THF (50 ml) was reacted for 3 h under nitrogen. The excess of $LiAlH_4$ was destroyed by adding $Na_2SO_4.10H_2O$ (0.50 g) and additional stirring for 16 h at room temperature. The salts were filtered off and the solvent was evaporated to give 4-(2-hexyloxyphenoxy)butylamine **4–4** (4.70 g, 98%). The amine was used directly for the synthesis of **5-nXm** without any further purification. M.p. 80°C. ^{1}H NMR: δ 6.86 (4H, s, ArH), 4.00–3.94 (4H, m, OCH_2), 3.74 (2H, broad s, NH_2), 2.85 (2H, t, J=6.4 Hz, CH_2NH_2), 1.90–1.30 (12H, m, CH_2), 0.87 (3H, t, J=5.2 Hz, CH_3). ^{13}C-NMR: δ 148.97, 148.64 (1,2-ArC–O), 121.23, 120.89 (3,6-ArC–H), 113.95, 113.62 (4, 5-ArC–H), 69.02, 68.75 (OCH_2), 41.12 (CH_2NH_2), 31.53–22.60 (CH_2), 14.01 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{16}H_{27}NO_2$, 265.2042; found, 265.2034.

The other compounds **4-n** were prepared similarly.

2.2.4. 1-Ethyl-3-(4-[2-hexyloxyphenoxy]butyl)urea, 5-4U2. A solution of ethyl isocyanate (0.40 g, 5.63 mmol) in dry dichloromethane (10 ml) was slowly added to a vigorously stirred solution of 4-(2-hexyloxyphenoxy)butylamine **4–4** (0.79 g, 2.98 mmol) in dry dichloromethane (30 ml). The mixture was stirred at room temperature, under nitrogen for 12 h. The product was purified by column chromatography on silica gel eluting with dichloromethane–methanol (9:1) as eluent, yielding 0.46 g (46%) of **5-4U2**. ^{1}H NMR: δ 6.85 (4H, m, ArH), 5.36 (1H, bt, J=5.4 Hz, NH), 5.05 (1H, bt, J=5.4 Hz, NH), 3.96 (4H, t, J=6.6 Hz, OCH_2), 3.27–3.07 (4H, m, CH_2NH), 1.85–1.25 (12H, m, CH_2), 1.04 (3H, t, J=7.2 Hz, CH_3CH_2), 0.87 (3H, t, J=6.7 Hz, CH_3). ^{13}C NMR: δ 158.87 (C=O), 148.81 (1-ArC–O), 148.78 (2-ArC–O), 121.16 (3,6-ArC–H), 113.86 (5-ArC–H), 113.75 (4-ArC–H), 69.28 (OCH_2), 68.92 (OCH_2), 39.90 (CH_2NH), 35.01–22.62 (CH_2), 15.55 (CH_3), 14.03 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{19}H_{32}N_2O_3$, 336.2413; found, 336.2417.

The other compounds **5-nUm** were prepared similarly.

2.2.5. 1-Ethyl-3-(4-[2-hexyloxyphenoxy]butyl)thiourea, 5-4T2. A mixture of 4-(2-hexyloxyphenoxy)butylamine **4–4** (4.20 g, 16.0 mmol) and ethyl isothiocyanate (1.68 g, 19.0 mmol) in dry dichloromethane (40 ml) was stirred for 3 h under nitrogen at room temperature. After

completion of the reaction the solvent was evaporated under vacuum and the resulting yellow oil was purified by column chromatography using dichloromethane with 0.5% methanol as eluent, yielding 4.19 g (75%) of **5-4T2**. ^{1}H NMR: δ 6.88 (4H, s, ArH), 6.45 (1H, bt, NH), 6.14 (1H, bt, NH), 4.04–3.94 (4H, m, OCH_2), 3.61 (2H, q, J=5.4 Hz, CH_3CH_2NH), 3.40 (2H, bt, $NHCH_2CH_2$), 1.89–1.29 (12H, m, CH_2), 1.10 (3H, t, J=7.3 Hz, CH_3CH_2), 0.87 (3H, t, J=6.3 Hz, CH_3). ^{13}C NMR: δ 181.19 (C=S), 148.44 (1-ArC–O), 148.26 (2-ArC–O), 121.32 (6-ArC–H), 121.09 (3-ArC–H), 113.43 (4,5-ArC–H), 69.09, 69.04 (OCH_2), 53.36, 43.82 (CH_2NH), 38.93–22.51 (CH_2), 14.09 (CH_3), 13.91 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{19}H_{32}N_2O_2S$, 352.2184; found, 352.2186.

The other compounds **5-nTm** were prepared similarly.

2.2.6. Propionic acid (4-[2-hexyloxyphenoxy]butyl)amide, 5-4A2. A mixture of 4-(2-hexyloxyphenoxy)butylamine **4–4** (1.15 g, 4.33 mmol) and propionyl chloride (0.35 g, 3.80 mmol) in dry dichloromethane (15 ml) was stirred for 3 h under nitrogen at room temperature. After completion of the reaction, the solvent was evaporated and the resulting yellow oil was purified by column chromatography, using dichloromethane–methanol (9:1) as eluent, yielding 0.96 g (79%) of **5-4A2**. ^{1}H NMR: δ 6.87 (4H, s, ArH), 6.02 (1H, broad s, NH), 4.03–3.95 (4H, dt, J=6.7 Hz, OCH_2), 3.33 (2H, q, J=6.1 Hz, CH_2NHCO), 2.16 (2H, q, J=7.5 Hz, $COCH_2CH_3$), 1.88–1.29 (12H, m, CH_2), 1.12 (3H, t, J=7.6 Hz, CH_3CH_2), 0.88 (3H, t, J=7.6 Hz, CH_3). ^{13}C NMR: δ 174.00 (C=O), 148.85 (1-ArC–O), 148.55 (2-ArC–O), 121.17 (6-ArC–H), 120.92 (3-ArC–H), 113.65 (5-ArC–H), 113.42 (4-ArC–H), 68.93 (OCH_2), 68.69 (OCH_2), 38.94 (CH_2NH), 31.51–22.56 (CH_2), 13.96 (CH_3), 9.95 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{19}H_{31}NO_3$, 321.2304; found, 321.2303.

The other compounds **5-nAm** were prepared similarly.

2.2.7. 1-Ethyl-3-(4-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]butyl)urea, 8-4U2. A mixture of 1-ethyl-3-(4-[2-hexyloxyphenoxy]butyl)urea **5-4U2** (0.33 g, 0.98 mmol), 0.81 g (1.46 mmol) biphenyl **7** and iron(III)chloride (1.00 g) in dry dichloromethane (40 ml) was stirred for 35 min under nitrogen at room temperature. Then the reaction was quenched with 100 ml of cold methanol. After filtration, the gray precipitate was purified by column chromatography using dichloromethane-methanol (2.5% methanol). Subsequent recrystallization from methanol gave 0.51 g (60%) of **8-4U2**. ^{1}H NMR: δ 7.82 (6H, m, ArH), 4.85 (2H, bs, NH), 4.22 (12H, t, J=6.5 Hz, OCH_2), 3.34 (2H, t, J=6.3 Hz, $NHCH_2$), 3.19–3.15 (2H, q, J=7.2 Hz, CH_3CH_2NH), 2.00–1.24 (44H, m, CH_2), 1.07 (3H, t, J=7.2 Hz, CH_2CH_3), 0.92 (15H, t, J=7.0 Hz, CH_3). ^{13}C NMR: δ 157.35 (C=O), 149.06–148.38 (2,3,6,7,10,11-ArC–O), 123.70–123.45 (ArC–C), 107.40–106.76 (ArC–H), 69.73–69.31 (OCH_2), 40.18 (CH_2NH), 35.28–22.65 (CH_2), 15.45, 14.04 (CH_3). MS (Maldi-tof) $[M]^{+\bullet}$: calculated for $C_{55}H_{86}N_2O_7$: 886.64; found 886.66.

The other compounds **8-nXm** were prepared similarly.

2.2.8. 1-Hexyl-3-(6-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]hexyl)urea, 8-6U6. ^{1}H NMR: δ 7.82 (6H, s, ArH), 4.22 (12H, t, J=6.5 Hz, OCH_2), 3.21–3.08 (6H, m, $2\times CH_2NH$, $2\times NH$), 2.00–1.86 (12H, m, OCH_2CH_2), 1.58–1.23 (44H, m, CH_2), 0.96–0.80 (18H, m, CH_3). ^{13}C NMR: δ 158.27 (C=O), 148.95, 148.92, 148.89, 148.73, 148.69 (2,3,6,7,10,11-ArC–O), 123.58, 123.53, 123.45 (ArC–C), 107.32, 107.16 (ArC–H), 69.73, 69.60, 69.30 (OCH_2), 40.53, 40.30 (CH_2NH), 31.64–22.52 (CH_2), 14.02, 13.97 (CH_3). MS $[M\text{-}NH_2C_6H_{13}]^{+\bullet}$: calculated for $C_{55}H_{83}NO_7$, 869.6170; found, $[M\text{-}NH_2C_6H_{13}]^{+\bullet}$: 869.6142.

2.2.9. 1-Hexyl-3-(10-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]decyl)urea, 8-10U6. ^{1}H NMR: δ 7.82 (6H, s, ArH), 4.53 (2H, bs, $2\times NH$), 4.22 (12H, t, J=6.5 Hz, OCH_2), 3.10–3.08 (4H, bq, J=5.1 Hz, $2\times CH_2NH$), 2.00–1.86 (12H, m, OCH_2CH_2), 1.60–1.24 (52H, m, CH_2), 0.96–0.82 (18H, m, CH_3). ^{13}C NMR: δ 158.40 (C=O), 148.85 (2,3,6,7,10,11-ArC–O), 123.50 (ArC–C), 107.18 (ArC–H), 69.61 (OCH_2), 40.48 (CH_2NH), 31.66–22.64 (CH_2), 14.04 (CH_3). MS $[M]^{+\bullet}$: calculated for $C_{65}H_{106}N_2O_7$, 1026.8000; found, 1026.8044.

2.2.10. 1-Methyl-3-(3-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]propyl)thiourea, 8-3T1. ^{1}H NMR: δ 7.85–7.80 (6H, m, ArH), 6.77, 6.39 (2H, bs, $2\times NH$), 4.35 (2H, t, J=5.6 Hz, OCH_2), 4.27–4.17 (10H, m, OCH_2), 3.83 (2H, broad signal, CH_2NH), 2.98 (3H, d, J=4.7 Hz, $NHCH_3$), 2.21 (2H, m, $OCH_2CH_2CH_2NH$), 2.00–1.90 (10H, m, OCH_2CH_2), 1.62–1.54 (10H, m, CH_2), 1.43–1.42 (20H, m, CH_2), 0.98–0.95 (15H, m, CH_3). ^{13}C NMR: δ 182.70 (C=S), 149.20–147.60 (2,3,6,7,10,11-ArC–O), 124.11–123.17 (ArC–C), 107.68–106.61 (ArC–H), 70.11–69.47 (OCH_2), 42.50 (CH_2NH), 31.67–31.03 (CH_2), 30.17 (CH_3NH), 29.66–29.33 (CH_2), 28.84 ($OCH_2CH_2CH_2NH$), 25.83–22.63 (CH_2), 14.03 (CH_3). MS (Maldi-tof) $[M\text{-}NH_2CH_3]^{+\bullet}$: calculated for $C_{52}H_{77}NO_6S$, 843.55; found, $[M\text{-}NH_2CH_3]^{+\bullet}$ 843.24.

2.2.11. 1-Ethyl-3-(3-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]propyl)thiourea, 8-3T2. ^{1}H NMR: δ 7.86–7.81 (6H, m, ArH), 6.70, 6.20 (2H, bs, 2 × NH), 4.35 (2H, t, J=5.2 Hz, OCH_2CH$_2$CH$_2$NH), 4.27–4.23 (10H, m, OCH$_2$), 3.84 (2H, broad signal, CH_2NH), 3.44 (2H, m, NHCH_2CH$_3$), 2.21 (2H, m, NHCH$_2$CH_2CH$_2$O), 2.00–1.91 (10H, m, OCH$_2$CH_2), 1.61–1.42 (30H, m, CH$_2$), 1.14 (3H, t, J=7.2 Hz, NHCH$_2$CH_3), 0.98–0.95 (15H, m, CH$_3$). ^{13}C NMR: δ 181.70 (C=S), 149.20–147.71 (2,3,6,7,10,11-ArC–O), 124.13–123.18 (ArC–C), 107.80–106.69 (ArC–H), 69.76–69.49 (OCH$_2$), 68.24 (OCH$_2$), 42.27, 39.05 (CH$_2$NH), 31.67–29.33 (CH$_2$), 28.86 (OCH$_2$*C*H$_2$CH$_2$NH), 25.83–22.63 (CH$_2$), 14.15 (CH$_3$), 14.03 (CH$_3$). MS (Maldi-tof) [M+H]$^{+\bullet}$: calculated for $C_{54}H_{85}N_2O_6S$, 889.61; found, [M+H]$^{+\bullet}$ 889.57.

2.2.12. 1-Methyl-3-[4-(3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy)butyl]thiourea, 8-4T1. ^{1}H NMR: δ 7.86–7.83 (6H, m, ArH), 6.38, 6.14 (2H, broad m, 2 × NH), 4.34–4.23 (12H, m, OCH$_2$), 3.72 (2H, m, CH$_2$CH_2NH), 2.98 (3H, m, NHCH_3), 2.04–1.92 (14H, m, CH$_2$), 1.62–1.38 (30H, m, CH$_2$), 0.97–0.94 (15H, m, CH$_3$). ^{13}C NMR: δ 182.57 (C=S), 149.24–148.09 (2,3,6,7,10,11-ArC–O), 123.82–123.36 (ArC–C), 107.52–106.58 (ArC–H), 69.87–69.56 (OCH$_2$), 44.09 (CH$_2$NH), 31.69 (CH$_3$NH), 31.63–29.25 (CH$_2$), 26.75, 26.15 (OCH$_2$*C*H$_2$*C*H$_2$CH$_2$NH), 25.86–22.66 (CH$_2$), 14.05 (CH$_3$). MS (Maldi-tof) [M+H]$^{+\bullet}$: calculated for $C_{54}H_{85}N_2O_6S$, 889.61; found, [M+H]$^{+\bullet}$ 889.87.

2.2.13. 1-Ethyl-3-(4-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]butyl)thiourea, 8-4T2. ^{1}H NMR: δ 7.82 (6H, s, ArH), 6.31 (1H, bs, NH), 6.00 (1H, bs, NH), 4.30–4.19 (12H, m, OCH$_2$), 3.72 (2H, q, CH$_3$CH_2NH), 3.39 (2H, bt, NHCH_2CH$_2$), 1.97–1.24 (44H, m, CH$_2$), 1.10 (3H, t, J=7.2 Hz, CH$_2$CH_3), 0.92 (15H, t, J=6.8 Hz, CH$_3$). ^{13}C NMR: δ 181.41 (C=S), 149.25–148.09 (2,3,6,7,10,11-ArC–O), 123.83–123.36 (ArC–C), 107.54–106.59 (ArC–H), 69.88–69.53 (OCH$_2$), 44.02, 39.06 (CH$_2$NH), 26.68, 26.21 (OCH$_2$CH$_2$CH$_2$CH$_2$NH), 25.86–22.66 (CH$_2$), 14.19 (CH$_3$), 14.05 (CH$_3$). MS (Maldi-tof) [M+H]$^{+\bullet}$: calculated for $C_{55}H_{87}N_2O_6S$, 903.63; found, [M+H]$^{+\bullet}$ 903.38.

2.2.14. 1-Ethyl-3-(10-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]decyl)thiourea, 8-10T2. ^{1}H NMR: δ 7.82 (6H, s, ArH), 5.74 (2H, bs, NH), 4.22 (12H, t, J=6.5 Hz, OCH$_2$), 3.44–3.34 (4H, m, CH_2NH), 1.96–1.86 (12H, m, OCH$_2$CH_2), 1.60–1.00 (44H, m, CH$_2$), 1.17 (3H, t, J=7.2 Hz, CH_3CH$_2$NHCS), 0.89 (15H, t, J=7.1 Hz, CH$_3$). ^{13}C NMR: δ 181.30 (C=S), 148.96, 148.91 (2,3,6,7,10,11-ArC–O), 123.56 (ArC–C), 107.24 (ArC–H), 69.67 (OCH$_2$), 44.39, 39.12 (2 × *C*H$_2$NHCS), 31.71–22.69 (CH$_2$), 14.27, 14.09 (CH$_3$). MS (Maldi-tof) [M-(NH-CS-C$_2$H$_5$)]$^{+\bullet}$: calculated for $C_{58}H_{92}NO_6$, 899.69; found, [M-(NH-CS-C$_2$H$_5$)]$^{+\bullet}$ 899.50.

2.2.15. Propionic acid (4-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]butyl)amide, 8-4A2. ^{1}H NMR: δ 7.83–7.81 (6H, m, ArH), 6.21 (1H, bs, NH), 4.22 (12H, t, J=6.5 Hz, OCH$_2$), 3.43 (2H, q, J=6.0 Hz, CH_2NHCO), 2.24 (2H, q, J=7.6 Hz, CH$_3$CH_2CO), 2.02–1.36 (44H, m, CH$_2$), 1.15 (3H, t, J=7.6 Hz, CH$_3$), 0.92 (15H, t, J=7.0 Hz, CH$_3$). ^{13}C NMR: δ 173.90 (C=O), 148.98, 148.52, 148.28 (2,3,6,7,10,11-ArC–O), 123.65, 123.42 (ArC–C), 107.36–106.61 (ArC–H), 69.63–69.10 (OCH$_2$), 39.12 (CH$_2$NH), 31.66–22.65 (CH$_2$), 14.05 (CH$_3$), 9.98 (CH$_3$). MS [M]$^{+\bullet}$: calculated for $C_{55}H_{85}NO_7$, 871.6326; found, 871.6309.

2.2.16. Octanoic acid (10-[3,6,7,10,11-pentakishexyloxytriphenylen-2-yloxy]decyl)amide, 8-10A7. ^{1}H NMR: δ 7.82 (6H, s, ArH), 5.51 (1H, bt, J=4.2 Hz, NH), 4.22 (12H, t, J=6.5 Hz, OCH$_2$), 3.18 (2H, q, J=6.6 Hz, CH_2NH), 2.12–1.25 (68H, m, CH$_2$), 0.96–0.75 (18H, m, CH$_3$). ^{13}C NMR: δ 173.06 (C=O), 148.97 (2,3,6,7,10,11-ArC–O), 123.60 (ArC–C), 107.31 (ArC–H), 69.69 (OCH$_2$), 39.49 (CH$_2$NH), 36.87 (*C*H$_2$CO), 31.72–22.63 (CH$_2$), 14.08 (CH$_3$). MS [M]$^{+\bullet}$: calculated for $C_{66}H_{107}NO_7$, 1025.8048; found, 1025.8073.

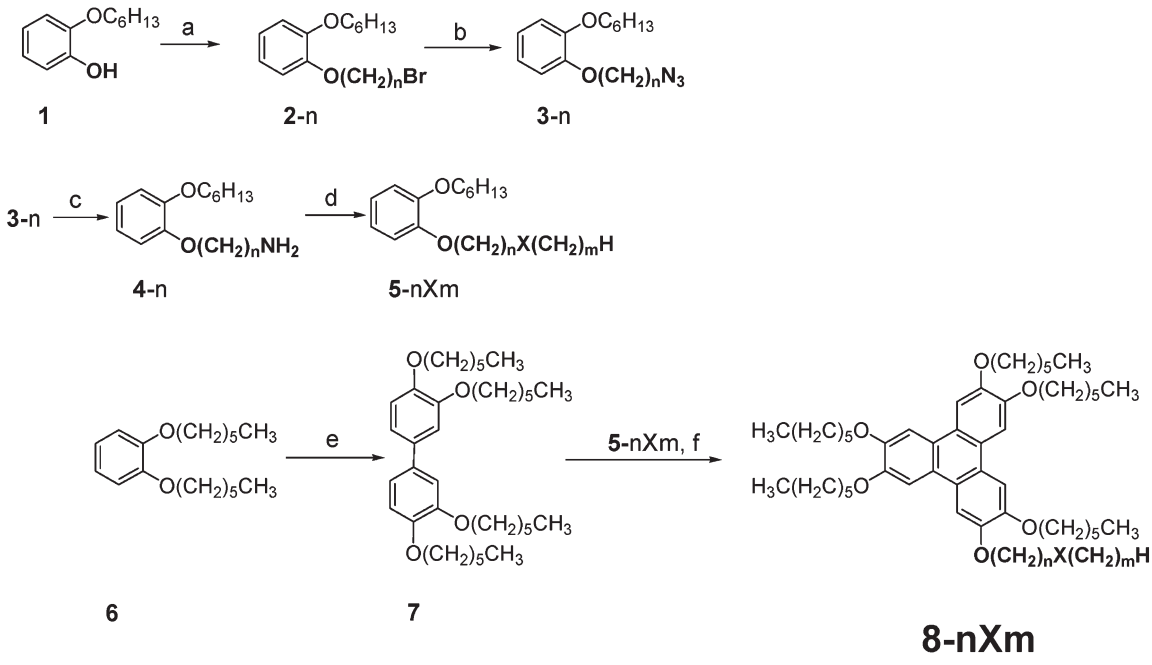
3. Results and discussion

3.1. *Synthesis*

The synthesis of compounds **8-nXm** is illustrated in scheme 1. In the final reaction step an oxidative coupling between biphenyl **7** and phenyl derivatives **5-nXm** is performed using $FeCl_3$ in CH_2Cl_2 under anhydrous conditions. The biphenyl derivative **7** was synthesized as previously described [11]. Reaction of catechol with 1-bromohexane in a 1:1 ratio yielded both 2-hexyloxyphenol **1** (35%) and 1,2-bis(hexyloxy)benzene **6** (51%), which were separated by column chromatography.

2-Hexyloxyphenol **1** was reacted with a dibromoalkane to give compounds **2-n**. In the next step, the bromo derivatives **2-n** were reacted with sodium azide to give azido derivatives **3-n** in relatively high yield. Subsequently, the azides were reduced with $LiAlH_4$ to give the amine derivatives **4-n**. Reaction of the amines with the proper alkyl isocyanates, alkyl thioisocyanates or acid chlorides gave the corresponding ureas, thioureas and amides **5-nXm**.

It should be stressed that rigorous anhydrous conditions are required for handling anhydrous $FeCl_3$. The presence of small traces of water gives rise to the



Scheme 1. Synthesis of compounds **8-nXm**: (a) $Br(CH_2)_nBr$, 2-butanone, K_2CO_3; (b) NaN_3, ethanol; (c) $LiAlH_4$, THF, $Na_2SO_4.10H_2O$; (d) $CH_3(CH_2)_{m-1}NCO$ (for ureas), $CH_3(CH_2)_{m-1}COCl$ (for amides) or $CH_3(CH_2)_{m-1}NCS$ (for thioureas), CH_2Cl_2; (e) ICl, $CHCl_3$; Cu, heat; (f) $FeCl_3$, CH_2Cl_2, MeOH.

formation of a mixture of several triphenylene isomers due to unselective ether cleavage reactions at the HAT6 core. These isomers are difficult to separate by column chromatography.

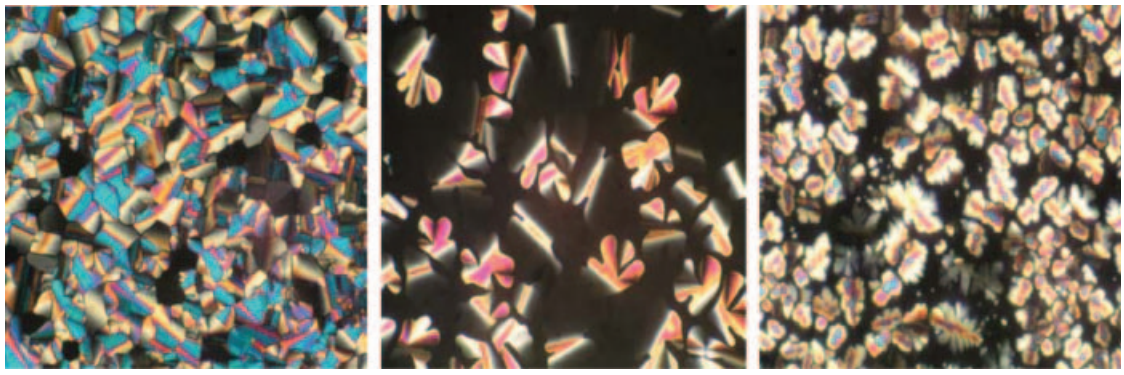
3.2. *Characterization*

The structures and purity of the synthesized products were confirmed by ^1H NMR, ^{13}C NMR, mass spectroscopy and thin layer chromatography (TLC). For the exact mass determination of **8-3T1**, **8-10T2** and **8-6U6** the molecular ion peak was not observed. Instead, fragments were observed that were also in agreement with the proposed structures. The thermotropic properties of compounds **8-nXm** were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), temperature-dependent FTIR spectroscopy and X-ray diffraction (XRD).

POM shows that not all synthesized compounds exhibit mesophase formation. The compounds with an amide or urea group do not show liquid crystalline behaviour. However, most of the compounds with a thiourea group show columnar discotic liquid crystalline phases. Compounds **8-3T1**, **8-3T2** and **8-4T1** are enantiotropic, whereas **8-4T2** shows monotropic behaviour. The thiourea with the longest spacer, **8-10T2**, again shows no mesophase formation.

The textures of the liquid crystalline thiourea compounds (**8-3T1**, **8-3T2**, **8-4T1**) are typical for a hexagonal columnar discotic mesophase (Col_h) (figure 2). The DSC data for all **8-nXm** compounds are shown in table 1. Within the series of compounds that have a butyl spacer and an ethyl terminal group, the urea derivative **8-4U2** has the highest melting point (134°C), followed by the amide derivative **8-4A2** (112°C) and then by the thiourea derivative **8-4T2** (85°C). A similar trend is observed for all present compounds: the urea derivatives show the highest melting points followed by the amide and then by the thiourea compounds. This thermal behaviour corresponds with the H-bonding strength, which is the strongest between urea groups [23], weaker between amide groups (one H-bond less than between urea groups), and even weaker between thiourea groups [24]. From this point of view, the H-bonding interactions between urea or amide groups present in the alkyl tail turned out to be detrimental for the formation of a mesophase.

For this series of compounds the H-bonding interactions appear to be a perturbing factor for the π–π stacking between the triphenylene cores, which in fact is essential for obtaining the columnar discotic mesophase [25]. The four thiourea compounds that show liquid crystalline behaviour were also studied by X-ray powder diffraction. An example is shown in figure 3. The diffractograms are indicative for a hexagonal columnar phase (Col_h), as is very often observed for triphenylenes [26]. The {100} reflection is very strong due to



(*a*) (*b*) (*c*)

Figure 2. Polarized optical microphotographs of (a) **8-3T1** at 50°C, (b) **8-3T2** at 63°C and (c) **8-4T1** at 57°C, all showing a Col_h phase.

alignment of the columns parallel to the glass substrate. The {001} reflection, corresponds to the distance between the triphenylene disc, while the additional broad reflection corresponds to the average alkyl distances. As can be seen in table 2, the intercolumnar distance slightly increases with increasing total tail length, as expected [11]. Compared to the corresponding alkyl derivatives with the same total tail length the intercolumnar distance is about 0.6 Å shorter. This may be caused by intermolecular hydrogen bonding that has a compacting effect on the fluid alkyl tails of these compounds.

Comparison of these thiourea compounds with molecules having only methylene moieties in the tails [11], shows that the melting points in the thiourea compounds are higher and the isotropization temperatures are lower. It therefore seems that H-bonding in these materials stabilizes the crystalline state and destabilizes the liquid crystalline ordering. This trend seems to hold also for the amide and urea derivatives; the melting points become higher for compounds that give stronger H-bonding, and for these two classes of materials the liquid crystallinity even disappears completely.

Table 1. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}, in square brackets) of the triphenylene derivatives **8-nXm** obtained from DSC at 10°C min^{-1}.

Compound	M.p.	Col_h–I
8-3T1	63 [30]	75 [3]
8-3T2	61 [28]	69 [3]
8-4T1	63 [40]	63 [3]
8-4T2	85 [31]	(54 [2])
8-10T2	37 [35]	
8-4A2	112 [53]	
8-10A7	75 [42]	
8-4U2	134 [44]	
8-6U6	91 [36]	
8-10U6	77 [35]	

The H-bonding in **8-nXm** molecules was also investigated by FTIR spectroscopy [27]. FTIR spectra for three different triphenylene derivatives (**8-10U6**, **8-4A2** and **8-3T2**) with different H-bonding groups were recorded at room temperature using dry powder samples in KBr and as solutions in $CDCl_3$. In all cases ν(N–H) is significantly lower in the solid state than in $CDCl_3$ solution. For **8-10U6** ν(N–H) is 3344 cm^{-1} in KBr and 3448 cm^{-1} in $CDCl_3$; for **8-4A2**, ν(N–H) is 3305 cm^{-1} in KBr and 3451 cm^{-1} and 3409 cm^{-1} in $CDCl_3$; and for **8-3T2**, ν(N–H) is 3285 cm^{-1} in KBr and 3430 cm^{-1} and 3363 cm^{-1} in $CDCl_3$. These differences show the presence of H-bonds in the solid state.

In addition, temperature-dependent FTIR spectra of compound **8-3T2** (neat) were recorded upon cooling from 85°C, which is 25°C higher than its isotropization point, to room temperature (figure 4). At 85°C the free

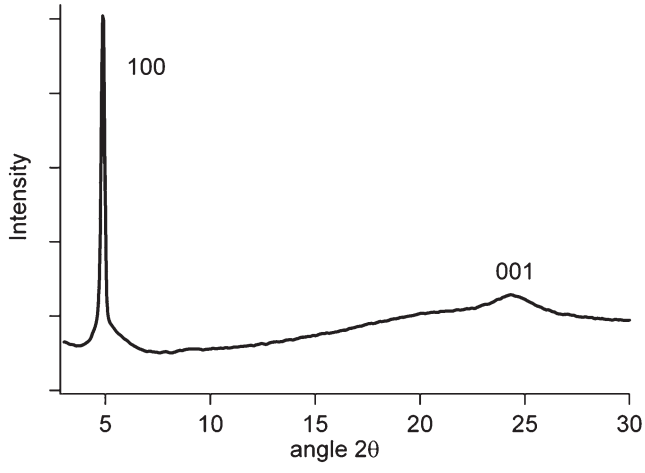


Figure 3. X-ray diffractogram of thiourea derivative **8-3T1** at 60°C.

Table 2. X-ray data for the liquid crystalline thiourea derivatives and HAT6.

Compound	Phase	Interdisc distance/Å	*d*-spacing/Å	Intercolumn distance[a]/Å
HAT6	Col_h	3.61	18.34	21.17
8-3T1	Col_h	3.60	18.04	20.83
8-3T2	Col_h	3.60	18.20	21.01
8-4T1	Col_h	3.65	18.20	21.01
8-4T2	Col_h	3.95	18.40	21.24

[a]Intercolumn distance is $2/\sqrt{3} \times d$.

N–H groups are indicated by a small peak at 3350 cm^{-1}, which indicated a somewhat weaker N–H bond than found for $CDCl_3$ solution (3363 cm^{-1}), but the wavenumber is higher than found for the solid state (3336 cm^{-1}). Upon cooling, the intensity of this peak decreases, whereas the peak at about 3285 cm^{-1} (indicative for H-bonding) increases in intensity. When H-bonding would be dominant in the liquid crystalline phase, the strongest change in both the intensity and the shifts of the peaks would be expected to occur at the isotropic to liquid crystalline transition. Here the changes are more gradual, although the phase transitions can be recognized as more abrupt changes. These results indicate that in these thiourea compounds hydrogen bonding is clearly present but not dominant in the columnar liquid crystalline phase. More important is the π–π stacking interaction. On the other hand, when the hydrogen bonding becomes stronger and starts to override the π–π stacking, as in the amide and urea compounds, the columnar ordering is not possible anymore.

Based on the properties of compounds **8-nXm**, a model for the intermolecular interactions emerges. A columnar mesophase is obtained for the combination of rigid central cores that display π–π stacking interactions, and flexible chains at the periphery. If the π–π stacking, which is vital for a columnar organization is disturbed, the mesophase range narrows or is completely suppressed. This last situation is observed in the case of urea and amide-containing triphenylene derivatives. In these two cases, the H-bonding interactions at one position in the peripheral tails strongly disturb the π–π stacking between the triphenylene discs, and therefore result in the loss of liquid crystallinity. Although hydrogen bonding also exists in the columnar phases of the thiourea compounds, it is too weak to considerably disrupt the π–π stacking between the triphenylene groups.

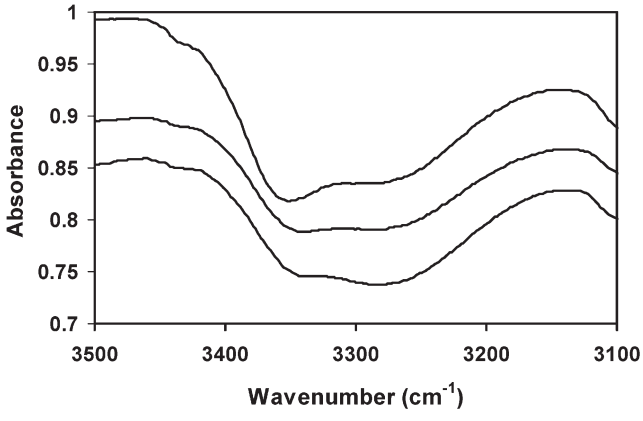


Figure 4. Temperature dependence of the ν(N–H) stretching vibration of the thiourea derivative **8-3T2** (from top to bottom 85, 55 and 35°C).

It was shown previously that asymmetry in the alkyl tail lengths can also be a disturbing factor for the formation of columnar phases for HAT derivatives [11]. Replacement of one of the six hexyloxy substituents of HAT6, with an alkoxy substituent with more than twelve carbon atoms, completely suppresses the liquid crystalline behaviour. This is most likely the reason that **8-10T2**, the thiourea compound with the longest tail, does not show liquid crystalline behaviour.

These results show that changing the structure of only one substituent around the triphenylene core can dramatically disturb the columnar organization. Similar results were found for HAT5 derivatives, for which bulky or polar substituents were also found to destabilize the columnar mesophase [28]. On the other hand, recent examples of HAT derivatives with H-bonding groups in three of their tails have shown that in those cases a significant stabilization of the columnar liquid crystalline phases can be obtained [19]. Therefore only a proper balance of interactions, such as H-bonding directly linked to the aromatic core [15], provides a good route to stabilize liquid crystalline columns.

4. Conclusions

Several novel triphenylene derivatives with urea, amide or thiourea groups in one of their tails have been synthesized. Among the new materials only the thiourea-containing triphenylenes (**8-3T1**, **8-3T2**, **8-4T1** and **8-4T2**) show a columnar hexagonal (Col_h) mesophase, whereas the urea and amide-containing triphenylenes do not possess a liquid crystalline phase. For these latter series, hydrogen bonding stabilizes the crystalline state and destabilizes the columnar liquid crystalline organization (higher melting points and lower liquid crystal to isotropic transitions). For the thiourea-containing triphenylenes, the π–π stacking interactions can overcome the destabilizing effects of

the relatively weak hydrogen bonding of the thiourea groups. In addition, the total length of the tail containing the hydrogen bond-forming group is also important for observing liquid crystallinity: if this tail becomes too long, liquid crystallinity is also lost.

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