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SUPRAMOLECULAR ARCHITECTURES OF C_3-SYMMETRICAL AND ASYMMETRICAL DISCOTICS

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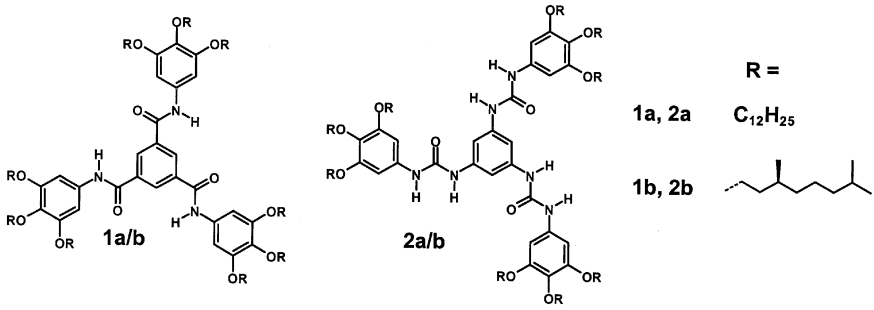
*Chiral (**3b**) and achiral (**3a**) C_3-symmetrical nitrogen centered amide disks were investigated with optical polarizing microscopy, differential scanning calorimetry and UV-Vis/circular dichroism spectroscopy. Similar to the carbonyl centered amide disks **1a/b**, only achiral compound **3a** shows order in the liquid crystalline phase. Using the same techniques, two asymmetrical mono amide bisurea disks were investigated, one containing 6 "chiral urea" groups (**4**) and the other containing 3 "chiral amide" centers (**5**). These compounds do show supramolecular aggregation in dilute apolar solutions, featuring hysteresis in experiments investigating thermoreversibility; similar to C_3-symmetrical trisurea compounds **2a/b**.*

Keywords: discotics; supramolecular architectures; CD-spectroscopy

INTRODUCTION

Self-assembled structures may find their application in either biology or materials science, since supramolecular architectures are well defined though reversible in nature [1,2,3]. Discotic molecules were found suitable building blocks for cylindrical architectures [4], and several examples of columnar liquid crystalline phases are known [5,6]. However, special demands on the directionality and strength of secondary interactions between disks have to be met to maintain these supramolecular columns in organogels [7,8], or even in dilute solution [9]. Next to the possibility to create cholesteric and ferroelectric liquid crystals, chirality was recognized as a new tool to study the self-assembly of the disks in diluted systems [10,11].

We reported on C_3-symmetrical discotics that form helical columnar structures in the solid state [12], in the gel phase [13], as well as in dilute solution [14]. In case of discotics based on gallic acid derivatives (Scheme 1), a large difference was found between the amide disks **1a/b** and the urea

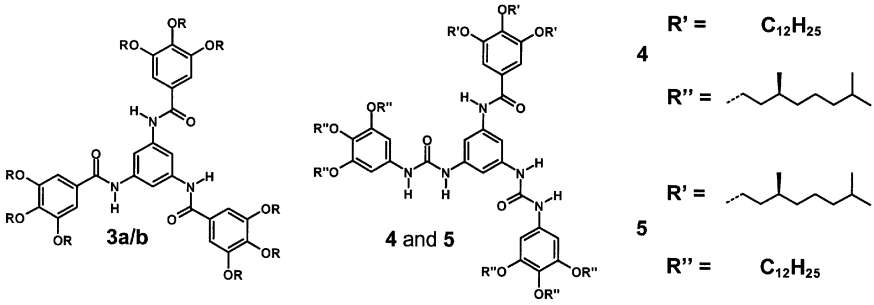


SCHEME 1 Chemical structures of carbonyl centered trisamides **1a/b** (left), and trisureas **2a/b** (right).

disks **2a/b**, illustrating that a minor structural variation can have a drastic effect on the delicate balance between intermolecular interactions needed for supramolecular aggregation [15]. "Gallic" carbonyl centered trisamides **1a/b** were not capable of retaining their columnar structure in apolar solution. Ordering was only found in the liquid crystalline phases of **1a/b**, and in the case of chiral disk **1b** only in a very small temperature window. On the other hand, the "gallic" trisurea **2a/b** did form rigid rod-like structures at concentrations as low as 10^{-5} M.

Urea hydrogen bonding is stronger than amide bonding, because ureas may display two hydrogen bonds, while amides have only one. Probably, this causes the difference in supramolecular aggregation between trisamide and trisurea molecules **1** and **2**. However, it could be argued that the connection of the hydrogen bonding groups to the central benzene ring rationalizes the difference. The hydrogen bonding groups of amide **1** are connected to the central core *via* the carbonyl group, while those of urea **2** are connected *via* the nitrogen atom. To rule out any influences caused by this difference in connectivity, nitrogen centered trisamides **3a/b** were synthesized and investigated (Scheme 2).

To better understand why trisamide disks **1** do not form columnar aggregates in dilute apolar solution and why trisurea disks **2** do, two asymmetrical "gallic" structures were investigated, each containing one amide and two urea groups. Mono amide bisurea disk **4** contains 6 chiral centers, which are connected to the central benzene ring *via* the urea groups, while mono amide bisurea disk **5** is equipped with 3 'chiral amide' functionalities. This enables us to investigate separately the aggregation of the amide or the urea groups of these asymmetrical disks with circular dichroism spectroscopy. From these data, information concerning the conformation of the asymmetrical disks in the supramolecular aggregate can be obtained.



SCHEME 2 Chemical structures of nitrogen centered trisamides **3a/b** (left), and mono amide bisureas **4** and **5** (right). R-groups of **3a/b** are similar to those of **1a/b** (see Scheme 1).

EXPERIMENTAL

General

All starting materials were obtained from commercial suppliers and used as received. The syntheses of the following compounds have been described previously: **1a/b** [15], **2a/b** [15], 3,4,5-tridodecyloxybenzoyl chloride/3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzoyl chloride [12], and 3,4,5-tridodecyloxybenzene isocyanate/3,4,5-tris((*S*)-3,7-dimethyloctyloxy) benzene isocyanate [16]. All moisture sensitive reactions were performed under an atmosphere of dry argon. Dry and ethanol-free dichloromethane was obtained by distillation from P_2O_5; dry tetrahydrofuran was obtained by distillation from Na/K/benzophenone; toluene was dried on Merck molsieves (4 Å); and triethylamine was dried over potassium hydroxide. Analytical thin layer chromatography was performed on Kieselgel F-254 precoated silica plates. Visualization was accomplished with UV light. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh or 230–400 mesh ASTM). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR or on a Varian Gemini, 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and carbon chemical shifts in ppm downfield from TMS using the resonance of the deuterated solvent as internal standard. Elemental analyses were carried out using a Perkin Elmer 2400. Matrix assisted laser desorption/ionization mass spectra were obtained using α-cyano-4-hydroxycinnamic acid as the matrix on a PerSeptive Biosystems Voyager-DE PRO spectrometer. IR spectra were measured on a Perkin Elmer 1600 FT-IR. Optical properties and melting points were determined

using a Jenaval polarization microscope with crossed polarizers equipped with a Linkham THMS 600 heating device. DSC spectra were obtained on a Perkin Elmer Pyris 1 DSC. UV/Vis spectra were recorded on a Perkin Elmer Lambda 40 UV/Vis spectrometer. CD spectra were recorded on a Jasco J-600 spectropolarimeter equipped with a Jasco PTC-348WI Peltier type temperature control system.

1,3,5-Tris-(3,4,5-tridodecyloxybenzoylamino)benzene (3a)

A solution of 3,4,5-tridodecyloxybenzoyl chloride (0.49 g, 0.81 mmol) in dichloromethane (10 ml) was added dropwise to a solution of di-amine **7a** (0.30 g, 0.38 mmol) and triethylamine (0.13 ml, 0.92 mmol) in dichloromethane (5 ml). After stirring overnight and evaporation of the dichloromethane, the crude product was purified using column chromatography (flash silica, gradient: chloroform/dichloromethane+0–0.5% v/v methanol, $R_f = 0$–0.3). Finally, white sticky solid **3a** (0.67 g, 83%) was obtained: ^{1}H-NMR ($CDCl_3$) δ 8.24 (NH, s, 3H), 8.10 (H-ortho, s, 3H), 7.05 (H′-ortho, s, 6H), 3.98 (OCH_2, m, 18H), 1.80 (OCH_2CH_2, m, 18H), 1.46 ($OCH_2CH_2CH_2$, m, 18H), 1.26 ($(CH_2)_8$, m, 144H), 0.88 (CH_3, m, 27H); ^{13}C-NMR ($CDCl_3$) δ 165.9, 153.3, 141.6, 139.2, 129.1, 107.1, 105.5, 73.5, 69.3, 31.9, 30.4, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 26.1, 26.1, 22.7, 14.1; IR (ATR): 3278, 2921, 2852, 1645, 1615, 1581, 1536, 1499, 1455, 1385, 1332, 1220, 1112, 1003, 859, 760, 721, 677 cm^{-1}; MALDI-TOF MS: calc.: 2093.81, found: 2116.63 (Na adduct); Analysis: calc.: $C_{135}H_{237}N_3O_{12}$ (2094.41): C, 77.42; H, 11.41; N, 2.01; found: C, 77.44; H, 10.66; N, 2.00.

1,3,5-Tris-[3,4,5-tris((S)-3,7-dimethyloctyloxy)benzoylamino]-benzene (3b)

Analogous to the previous procedure 3,4,5-tris-((*S*)-3,7-dimethyloctyloxy) benzoyl chloride (1.0 g, 1.7 mmol) and di-amine **7b** (0.56 g, 0.81 mmol), gave **3b** as a white sticky solid (1.18 g, 80%): ^{1}H-NMR ($CDCl_3$) δ 8.05 (H-ortho, s, 3H), 8.01 (NH, s, 3H), 7.08 (H′-ortho, s, 6H), 4.07 (OCH_2, m, 18H), 1.88-0.86 (alkyl H, m, 171H); ^{13}C-NMR ($CDCl_3$) δ 165.8, 153.4, 141.7, 139.2, 129.2, 106.7, 105.5, 71.8, 67.7, 39.4, 39.3, 37.5, 37.4, 37.3, 36.4, 29.8, 29.7, 28.0, 24.7, 22.7, 22.6, 22.6, 19.6, 19.6; IR (ATR): 3284, 2954, 2925, 2870, 1650, 1616, 1583, 1551, 1501, 1464, 1429, 1384, 1329, 1216, 1110, 1045, 994, 956, 859, 753, 735, 687 cm^{-1}; MALDI-TOF MS: calc.: 1841.52, found: 1864.59 (Na adduct); Analysis: calc.: $C_{117}H_{201}N_3O_{12}$ (1841.92): C, 76.30; H, 11.00; N, 2.28; found: C, 76.29; H, 10.46; N, 2.31.

N-{3,5-Bis-{3-[3,4,5-tris-((S)-3,7-dimethyloctyloxy)-phenyl]-ureido}-phenyl)-3,4,5-tridodecyloxy-benzamide (4)

A solution of 3,4,5-tris-((*S*)-3,7-dimethyloctyloxy)benzoyl azide (0.59 g, 0.96 mmol) in dry toluene (9 ml) was refluxed for 2 h. The mixture was cooled to 80°C, after which a solution of di-amine **7a** (0.30 g, 0.38 mmol) in dry toluene (7 ml) was added dropwise. After stirring overnight the toluene was evaporated and the product dissolved in dichloromethane (15 ml). The solution was cooled with ice. This gave a precipitate that yielded white sticky solid **4** (0.70 g, 93%) after filtration: ^{1}H-NMR ($CDCl_3/CH_3OH$) δ 8.97 (amide NH, s, 1H), 8.14 (urea NH, s, 2H), 7.75 (urea NH, s, 2H), 7.54 (H-ortho, d, 2H), 7.27 (H-ortho, bs, 1H), 7.08 (H′-ortho, s, 2H), 6.64 (H″-ortho, s, 4H), 3.98 (OCH_2, m, 18H), 1.86–0.83 (alkyl H, m, 183 H); ^{13}C-NMR ($CDCl_3/CH_3OH$) δ 166.7, 153.6, 153.1, 153.0, 141.2, 140.0, 138.9, 134.2, 133.9, 129.3, 105.7, 105.3, 98.6, 73.5, 71.7, 69.2, 67.2, 39.3, 39.2, 37.5, 37.3, 37.2, 36.4, 31.8, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 27.9, 26.0, 26.0, 24.7, 24.6, 22.6, 22.5, 22.5, 19.5, 19.3, 14.0; IR (ATR): 3319, 2954, 2923, 2854, 1638, 1603, 1555, 1504, 1457, 1427, 1383, 1329, 1224, 1117, 1003, 824, 754, 719 cm^{-1}; MALDI-TOF MS: calc.: 1955.64, found: 1978.22 (Na adduct); Analysis: calc.: $C_{123}H_{215}N_5O_{12}$ (1956.11): C, 75.53; H, 11.08; N, 3.58; found: C, 74.52; H, 10.39; N, 3.52.

N-{3,5-Bis-[3-(3,4,5-tridodecyloxyphenyl)-ureido]-phenyl}-3,4,5-tris-((S)-3,7-dimethyloctyloxy)-benzamide (5)

Analogous to the previous procedure 3,4,5-tridodecyloxybenzoyl azide (1.0 g, 1.4 mmol) and di-amine **7b** (0.47 g, 0.68 mmol) in combination with additional column chromatography (flash silica, dichloromethane+0–0.5% v/v methanol, $R_f = 0$–0.1) gave white/brown sticky solid **5** (1.2 g, 87%): ^{1}H-NMR (THF-*d*8) δ 9.27 (amide NH, s, 1H), 7.89 (urea NH, s, 2H), 7.56 (H-ortho, bs, 2H), 7.48 (urea NH, s, 2H), 7.34 (H-ortho, bs, 1H), 7.06 (H′-ortho, s, 2H), 6.56 (H″-ortho, s, 4H), 3.85 (OCH_2, m, 6H), 3.67 (OCH_2, m, 12H), 1.69-0.64 (alkyl H, m, 195 H); ^{13}C-NMR (THF-*d*8) δ 167.0, 155.0, 154.9, 154.5, 143.2, 142.6, 142.3, 137.4, 135.7, 132.2, 108.3, 105.7, 99.7, 74.6, 72.9, 70.6, 69.1, 41.4, 71.3, 39.6, 39.5, 38.6, 33.9, 32.5, 31.9, 31.8, 31.8, 31.8, 31.7, 31.6, 31.6, 31.4, 30.0, 28.3, 28.2, 26.8, 26.8, 24.6, 24.2, 24.1, 21.2, 21.0, 15.5; IR (ATR): 3288, 2954, 2922, 2853, 1644, 1604, 1557, 1503, 1467, 1425, 1384, 1333, 1225, 1117, 1004, 826, 757, 719 cm^{-1}; MALDI-TOF MS: calc.: 2039.73, found: 2039.85; Analysis: calc.: $C_{129}H_{227}N_5O_{12}$ (2040.27): C, 75.94; H, 11.21; N, 3.43; found: C, 74.69; H, 10.39; N, 3.38.

3,4,5-Tridodecyloxy-N-(3,5-dinitrophenyl)-benzamide (6a)

A solution of 3,4,5-tridodecyloxybenzoyl chloride (11.4 g, 16.4 mmol) in dry THF (150 ml) was added to 3,5-dinitroaniline (3.0 g, 16.4 mmol) and

triethylamine (2.8 ml, 19.7 mmol) in dry THF (150 ml). After stirring overnight at 75°C the solvent was evaporated and the product purified with column chromatography (silica, hexane/ethyl acetate 8/2, $R_f = 0.3$) in combination with recrystallisation from hexane/ethyl acetate 9/1 to remove minor impurities or washing with methanol to remove 3,5-dinitroaniline. Finally, yellow solid **6a** (11.2 g, 81%) was obtained: ^{1}H-NMR ($CDCl_3$) δ 8.94 (H-2, d, 2H), 8.78 (H-4, t, 1H), 8.46 (NHCO, s, 1H), 7.02 (H-2′, s, 2H), 4.01 (OCH_2, m, 6H), 1.79-1.72 (OCH_2CH_2, m, 6H), 1.44 ($OCH_2CH_2CH_2$, m, 6H), 1.26 ($(CH_2)_8$, m, 48H), 0.88 (CH_3, m, 9H); ^{13}C-NMR ($CDCl_3$) δ 166.0, 153.3, 148.8, 142.2, 140.5, 127.8, 119.6, 113.6, 105.8, 73.7, 69.5, 31.9, 30.3, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7, 14.1; Elemental analysis: calculated: $C_{49}H_{81}N_3O_8$ (840.19): C, 70.05; H, 9.72; N, 5.00; found: C, 70.45; H, 9.79; N, 4.86; IR (ATR): 3418, 2916, 2848, 1676, 1585, 1541, 1498, 1467, 1429, 1347, 1336, 1202, 1120, 989, 894, 750, 726 cm^{-1}; Analysis: calc.: $C_{49}H_{81}N_3O_8$ (840.19): C, 70.05; H, 9.72; N, 5.00; found: C, 70.45; H, 9.79; N, 4.86.

3,4,5-Tris-((S)-3,7-dimethyloctyloxy)-N-(3,5-dinitrophenyl)-benzamide (6b)

Analogous to the previous procedure 3,4,5-tris-((*S*)-3,7-dimethyloctyloxy) benzoyl chloride (8.8 g, 14.4 mmol) gave yellow solid **6b** (9.5 g, 87%): ^{1}H-NMR ($CDCl_3$) δ 8.94 (H-2, d, 2H), 8.77 (H-4, t, 1H), 8.43 (NHCO, s, 1H), 7.07 (H-2′, s, 2H), 4.05 (OCH_2, m, 6H), 1.89-0.86 (alkyl H, m, 57H); ^{13}C-NMR ($CDCl_3$) δ 166.0, 153.4, 148.8, 142.3, 140.5, 127.8, 119.6, 113.6, 105.8, 72.0, 67.8, 39.3, 39.2, 37.5, 37.3, 37.3, 36.3, 29.8, 29.7, 28.0, 24.7, 22.7, 22.6, 22.6, 22.6, 19.5; IR (ATR): 3282, 3105, 2954, 2927, 2870, 1662, 1582, 1546, 1499, 1466, 1429, 1383, 1341, 1212, 1116, 1074, 997, 902, 727 cm^{-1} Analysis: calc.: $C_{43}H_{69}N_3O_8$ (756.04): C, 68.31; H, 9.20; N, 5.56; found: C, 68.41; H, 8.77; N, 5.54.

N-(3,5-Diamino-phenyl)-3,4,5-tridodecyloxy-benzamide (7a)

The di-nitro **6a** (0.84 g, 1.0 mmol) was shaken for $5\frac{1}{2}$ h under hydrogen gas (150 ml, 6 mmol, 3 atm.) together with a 10% w/w palladium on carbon catalyst (50 mg, 0.050 mmol), ethanol (3 ml) and THF (22 ml). The reaction mixture was filtered over 3 paper filters to remove the catalyst. After column chromatography (flash silica, CH_2Cl_2+1% Et_3N+2% MeOH, $R_f = 0.3$) **7a** was obtained as a sticky white/green solid (0.66 g, 85%): ^{1}H-NMR ($CDCl_3$) δ 7.54 (NHCO, s, 1H), 7.00 (H-2′, s, 2H), 6.46 (H-2, d, 2H), 5.83 (H-4, t, 1H), 4.01 (OCH_2, m, 6H), 3.62 (NH_2, s, 4H), 1.80 (OCH_2CH_2, m, 6H), 1.46 ($OCH_2CH_2CH_2$, m, 6H), 1.26 ($(CH_2)_8$, m, 48H), 0.88 (CH_3, m, 9H); ^{13}C-NMR ($CDCl_3$) δ 165.7, 152.9, 148.0, 141.0, 139.8, 130.0, 105.7,

98.2, 98.0, 73.4, 69.2, 31.8, 30.3, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 26.0, 22.6, 14.0; IR (ATR): 3343, 2921, 2852, 1615, 1582, 1544, 1497, 1453, 1335, 1223, 1113, 1002, 829 cm^{-1}; Analysis: calc.: $C_{49}H_{85}N_3O_4$ (780.23): C, 75.43; H, 10.98; N, 5.39; found: C, 75.44; H, 10.57; N, 5.78.

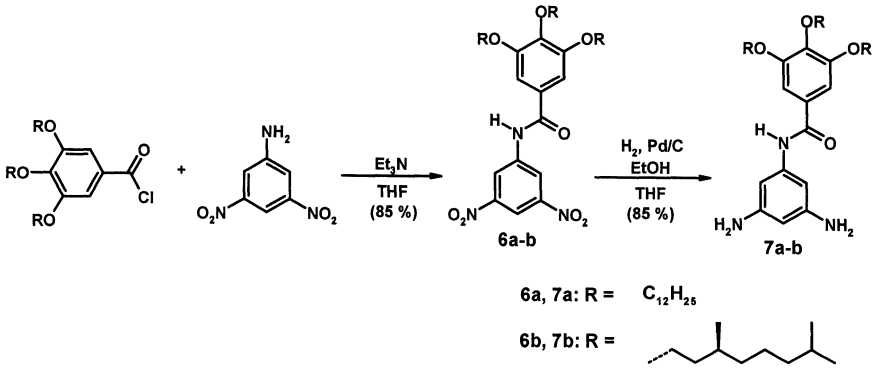
N-(3,5-Diamino-phenyl)-3,4,5-tris-((S)-3,7-dimethyloctyloxy)-benzamide (7b)

Analogous to the previous procedure di-nitro **6b** (2.0 g, 2.7 mmol) gave **7b** as a sticky white/brown solid (0.69 g, 92%): ^{1}H-NMR ($CDCl_3$) δ 7.51 (NHCO, s, 1H), 7.01 (H-2′, s, 2H), 6.46 (H-2, s, 2H), 5.83 (H-4, s, 1H), 4.05 (OCH_2, m, 6H), 3.62 (NH_2, s, 4H), 1.88-0.86 (alkyl H, m, 57H); ^{13}C-NMR ($CDCl_3$) δ 165.6, 153.2, 148.0, 141.3, 139.8, 130.2, 105.7, 98.3, 97.9, 71.7, 67.7, 39.3, 39.2, 37.5, 37.3, 37.3, 36.3, 30.3, 29.8, 29.6, 27.9, 25.6, 24.7, 24.7, 22.7, 22.6, 19.5; IR (ATR): 3346, 2954, 2926, 2870, 1616, 1582, 1546, 1497, 1453, 1383, 1334, 1226, 1113, 996, 833, 757, 684 cm^{-1}; MALDI-TOF MS: calc.: 695.56, found: 696.55.

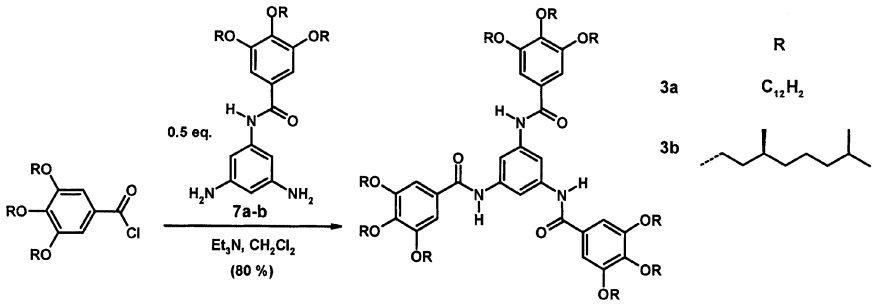
RESULTS

Synthesis

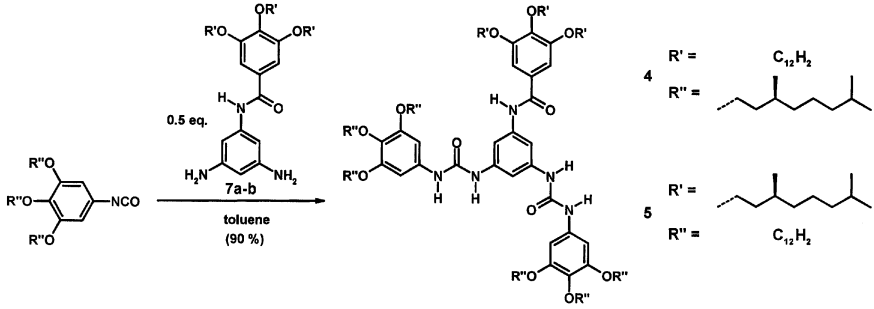
The synthesis of structures combining amide and urea functions requires introduction of asymmetry in the benzene-1,3,5-trisamine core. Therefore, 3,5-dinitroaniline was selected as starting compound. First the amine group was converted to an amide functionality using an acid chloride provided with solubilizing groups, derived from gallic acid [12], in the presence of triethylamine (Scheme 3). Achiral compound **6a** contains dodecyloxy



SCHEME 3 Synthesis of building blocks **6a/b** and **7a/b** based on 3,5-dinitroaniline.



SCHEME 4 Synthesis of nitrogen centered trisamide disks **3a/b**.



SCHEME 5 Synthesis of mono amide bisurea disks **4** and **5**.

chains, while in chiral compound **6b** (*S*)-3,7-dimethyloctyloxy chains are present. The nitro groups of di-nitro building block **6a/b** could be catalytically reduced with palladium on carbon, to give di-amine building block **7a/b** quantitatively. All compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy, elemental analysis, and mass spectrometry (see Experimental).

Di-amine building blocks **7a/b** could be converted into discotics upon 'end capping' with acid chlorides (in case of **3a/b**) or isocyanates (in case of **4** and **5**). Both achiral (**3a**) and chiral (**3b**) nitrogen centered trisamide disks were synthesized in good yield by treating di-amine **7a/b** with 2 equivalents 3,4,5-trialkoxybenzoyl chloride (Scheme 4). Similarly, mono amide bisurea disks **4** and **5** were obtained using 3,4,5-trialkoxybenzene isocyanate [16] (Scheme 5). Compounds **4** and **5** both contain one amide and two urea groups, but where **4** contains 6 chiral centers, which are connected to the core *via* the urea groups, **5** is equipped with 3 'chiral amide' functionalities.

FIGURE 1 Typical structure found in the liquid crystalline phase of nitrogen centered achiral amide disk **3a** (left) and crystals of chiral amide disk **3b** (right). (See Color Plates XVII & XVIII).

Optical Polarizing Microscopy and Differential Scanning Calorimetry

Nitrogen centered C_3-symmetrical amide disk **3a** shows liquid crystallinity (K: 28°C, 107 kJ/mol : M: 154°C, 53 kJ/mol : I), shown by the typical focal conic structures (Fig. 1). Chiral amide **3b** displays no liquid crystallinity and only one transition between the crystalline and isotropic phase was found (K: 87°C, 29 kJ/mol : I). Asymmetric disks **4** and **5** can be smeared and show birefringence from room temperature up to high temperatures, but no textures can be grown, as degradation occurs below the isotropization temperature (190°C).

Infrared Spectroscopy

The compounds were studied with IR spectroscopy by following the carbonyl stretch vibration in the solid state, and in 10^{-4} M heptane and chloroform solutions (Table 1). Carbonyl centered trisamide **1a** is not (completely) aggregated in dilute apolar solution, while trisurea **2a** is aggregated, as shown by similar carbonyl stretch vibrations in the solid state and in 10^{-4} M heptane solution. For nitrogen centered trisamide **3a** a value is found in heptane, intermediate between that of the aggregated (solid) state and the molecularly dissolved one (chloroform). When mono amide bisurea disk **4** was brought in heptane at a concentration of 10^{-2} M, a gel was formed. Unfortunately, no differentiation between the amide and urea signal was possible. Similar to trisamide **3a**, the wavenumbers of mono amide bisurea **4**, are not conclusive, at first glance.

However, in 10^{-2}–10^{-5} M tetrachloromethane solutions, infrared vibrations of **4** are similar to those in the solid state (1644 cm^{-1}), indicating supramolecular architectures. In chloroform and toluene the molecules are only partly hydrogen bonded at higher concentrations (10^{-2} and 10^{-3} M).

TABLE 1 Wavenumbers σ [cm^{-1}] of the Carbonyl Stretch Vibrations of Carbonyl Centered Trisamide **1a**, Trisurea **2a**, Nitrogen Centered Trisamide **3a**, and Mono Amide Bisureas **4** and **5** in the Solid State and in 10^{-4} M Heptane or Chloroform Solutions

Compound	1a[a]	2a[a]	3a	4
σ solid state	1682 1664	1641	1645	1638
σ 10^{-4} M heptane	1670 1650	1641	1656	1650
σ 10^{-4} M chloroform	1676	1644 (1711)	1672	1681

[a]See reference 15.

The (partial) aggregation in chloroform-*d*1 was confirmed by ^{1}H-NMR spectroscopy, where broad signals were observed, unlike the sharp signals obtained in chloroform-*d*1/methanol-*d*4 mixtures and in tetrahydrofuran-*d*8 (see Experimental). As the NMR results of disk **5** were comparable, the aggregation behavior in solution of **4** and **5** was judged similar at these concentrations.

CD Studies

C_3-symmetrical urea disks **2** form supramolecular aggregates in dilute apolar solutions, while C_3-symmetrical carbonyl centered amide disks **1** are not able to do so. Therefore, aggregate formation of the nitrogen centered C_3-symmetrical amide **3** and the asymmetrical mono amide bisurea disks **4** ("chiral urea") and **5** ("chiral amide"), was investigated with CD spectroscopy (Table 2).

Amide **3b** shows no Cotton effect in 10^{-4} M or 10^{-5} M heptane solutions. However, disks **4** and **5** do show remarkable effects (Fig. 2), resembling the signal of the C_3-symmetrical urea disk **2** in shape and intensity.

Temperature-dependent measurements with the C_3-symmetrical urea disk **2** revealed that the compound was highly thermally resistant (135°C) and that upon cooling 2 days were required for the original signal to restore. The Cotton effect of mono amide bisurea **4** in a 10^{-5} M heptane solution has disappeared completely at 55°C, and here also a large amount of hysteresis was observed (approximately 2 days). The Cotton effect of mono amide bisurea **5** in a 10^{-4} M heptane solution was only stable up to 30°C. Furthermore, upon cooling not only kinetic effects were observed but also some irreversibility.

TABLE 2 UV and CD Data of Carbonyl Centered Trisamide **1b**, Trisurea **2b**, Nitrogen Centered Trisamide **3b**, and Mono Amide Bisureas **4** and **5**; λ_{max} [nm] = the Absorption Band Most Towards the Red, and $\varepsilon/\Delta\varepsilon$ [l/mol·cm] = the Intensity of the Signal[a]

	UV-Vis		CD	
No.	λ_{max}	ε	λ_{max}	$\Delta\varepsilon$
1b[b]	308	2.1×10^4	–	–
2b[b]	259	5.1×10^4	275	−51.5
3b	286	4.8×10^4	–	–
4	261	4.0×10^4	265	−45.9
5	268	5.6×10^4	259	−45.1

[a]**1b**, **3b**, **4**, and UV of **5** measured at $\sim 10^{-5}$ M and CD of **5** at $\sim 10^{-4}$ M in heptane; **2b** measured at $\sim 10^{-5}$ M in dodecane.
[b]See reference 15.

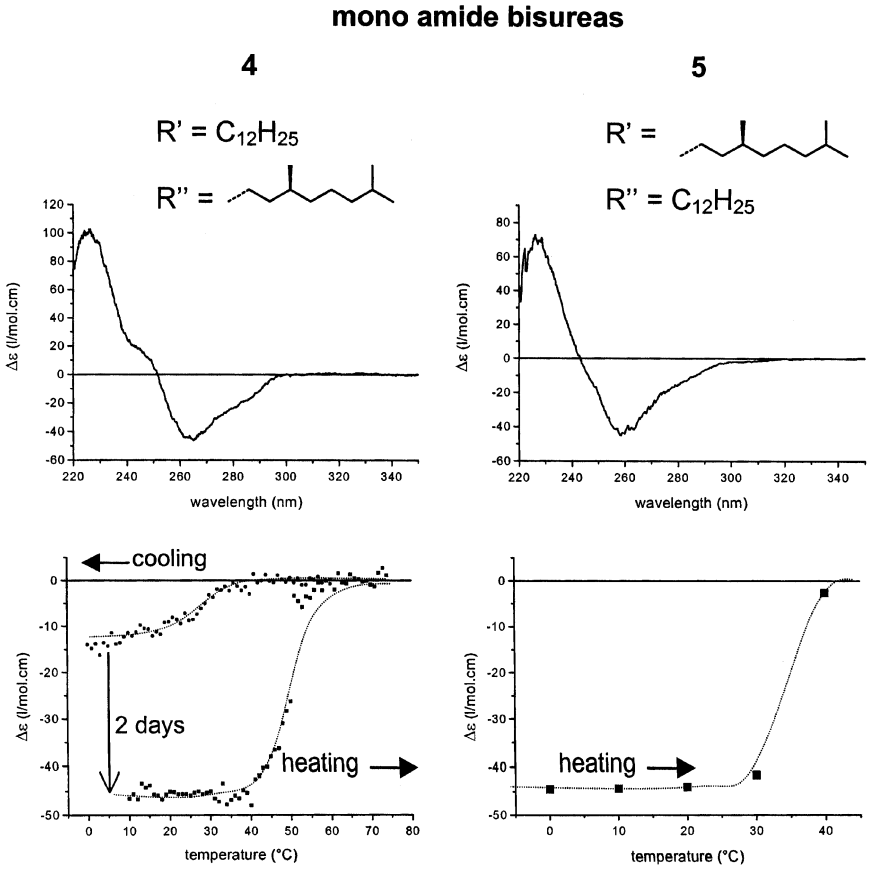


FIGURE 2 CD spectra and temperature-dependent data of mono amide bisurea disks **4** and **5**.

DISCUSSION

The absence of a liquid crystalline phase shown by nitrogen centered chiral amide **3b**, corresponds to the small liquid crystalline window shown by carbonyl centered chiral amide **1b** [15]. Achiral disks **1a** and **3a** both do form columnar liquid crystalline phases, but IR and CD measurements indicate that the (helical) columnar structure of disks **1** and **3** is not retained in apolar solution. The similar behavior of the carbonyl centered trisamides **1** and the nitrogen centered trisamides **3** indicates that the difference in supramolecular aggregation between trisamides **1** and trisureas **2** is not caused by the difference in connectivity of the hydrogen bonding groups to the central benzene ring (via the carbonyl group or the nitrogen atom, respectively). Clearly, in comparison to trisamide **1**, the stronger hydrogen bonding of the urea groups in trisurea **2** increases the tendency to form helical, columnar architectures.

Disk **4**, with two "chiral urea" groups and disk **5**, with one "chiral amide" group, both show Cotton effects in CD spectroscopy and their absorptions are similar in shape and maxima. This means that the urea, as well as the amide part, are capable of transferring chirality to the ensemble of chromophores present in the molecule, implying that urea ánd amide groups are hydrogen bonded. The binding of all three groups is confirmed by the fact that the Cotton effects of mono amide bisureas **4** and **5** resemble the effect displayed by trisurea **2b** judged from shape, maxima, intensity and hysteresis (Table 2). As the intensity of the Cotton effect of **4** (6 chiral centers) is similar to that of **2b** (9 chiral centers), one might speak of a 'sergeants and soldiers' effect [17]. Presumably, **4** and **5** adopt conformations in which the amide and urea groups are tilted with respect to the central benzene ring in a propellor-like way, just like the symmetrical urea disks **2** (Fig. 3).

From the presented CD data it does not become obvious whether the mono amide bisurea disks **4** and **5** are stacked urea by urea and amide by amide, or that also hydrogen bonds between amide and urea groups can occur. From mixing experiments between trisamides **1** and trisureas **2** it was deduced that chiral amide disks **1b** (that do not form aggregates by themselves) cannot induce chirality when they are mixed with achiral urea disks **2a** [15]. Assuming that this finding also applies to the asymmetrical disks **4** and **5**, this implies that only urea-urea and amide-amide hydrogen bonds occur. Presumably, aggregation is induced by the stronger urea interactions, and when in two superimposed disks two urea groups adopt a "bent" conformation, the amide groups of the two disks are interacting, and a third hydrogen bond is formed, inducing the thermodynamically most favorable state. In conclusion, in asymmetrical "gallic" compounds **4** and **5**

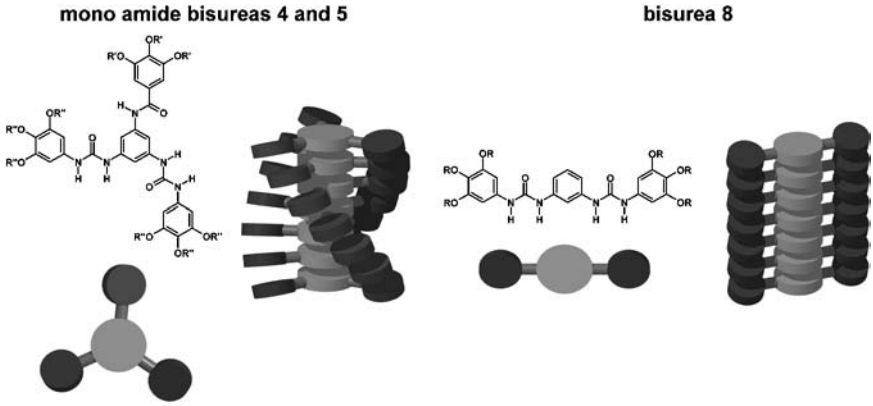


FIGURE 3 Schemetical representation of the supposed conformations of mono amide bisureas **4** and **5** (left) and bisurea **8** (right) in a supramolecular stack. R-groups of **8** are similar to those of **1b** (see Scheme 1). (See Color Plate XIX).

amide-amide hydrogen bonds can be formed, whereas in symmetrical "gallic" compounds **1** and **3**, this is not possible.

Although the Cotton effects of mono amide bisurea disks **4** and **5** are very similar, expression takes place at 10^{-5} M for "chiral urea" **4**, while for "chiral amide" **5** 10^{-4} M is needed. This could be rationalized by taking into account that **4** has 6 chiral centers and **5** has only 3, which renders transfer of chirality less efficient. However, when the UV maxima in 10^{-5} M solutions are examined (Table 2), it is clear that the maximum and the intensity of **4** ($\lambda_{max} = 261$ nm, $\varepsilon = 4.0 \times 10^4$ l/mol·cm) are significantly lower than those of **5** ($\lambda_{max} = 268$ nm, $\varepsilon = 5.6 \times 10^4$ l/mol·cm), meaning that **4** is aggregated stronger than **5** [18]. This confirms that the stacking of the amides is induced by the stacking of the ureas. Supposedly, a strong stack (a low UV maximum) is only obtained when a "propellor" is formed by rotation of both ureas and the amide in the same direction (either left or right). One can image that this is easier to reach when 2 "chiral ureas" leave only 1 choice (left or right) for 1 "achiral amide", than when 1 "chiral amide" has to overrule the stronger interactions of 2 "achiral ureas".

The concepts postulated above, correspond to the behavior shown by bisurea **8** [15] (Fig. 3). The bisurea aggregate produces a Cotton effect of a completely different shape and of much less intensity ($\lambda_{max} = 264$ nm, $\Delta\varepsilon = +15$ l/mol·cm). Furthermore, after the Cotton effect of bisurea **8** has disappeared at 80°C, no hysteresis occurs upon cooling. This contrasts with the time-dependent behavior of trisurea **2b**, and mono amide bisureas **4** and **5**. It is supposed that another Cotton effect implies another supra-

molecular architecture. Probably, the urea groups of bisurea **8** adopt a 'linear' conformation, unlike the 'bent' position of the urea groups in **2b**, **4**, and **5** (Fig. 3). This needs to be investigated further by for example AFM or SANS measurements.

CONCLUSIONS

The library of discotics is expanded with nitrogen centered trisamides **3a/b** and mono amide bisureas **4** and **5**. Carbonyl centered trisamides **1a/b** and nitrogen centered trisamides **3a/b** show the same aggregation behavior. Only achiral compounds **1**/**3a** form columnar liquid crystalline phases in a reasonable temperature window, and no aggregation takes place in solution. This shows that connectivity of the hydrogen bonding groups does not greatly alter the aggregation behavior, implying that the stronger urea hydrogen bonding causes the trisureas **2** to form rigid rod-like aggregates, while the weaker amide hydrogen bonding prevents the trisamides **1** to aggregate in dilute apolar solution.

Asymmetrical mono amide bisurea disks **4** and **5** do show supramolecular aggregates in dilute apolar solution. The Cotton effects themselves and their time-dependent thermoreversible nature correspond to the behavior of trisurea **2**, and do not coincide with that of bisurea **8**. Furthermore, aggregates of disks **4**, containing 6 chiral centers connected *via* the urea groups, are formed easier than aggregates of disks **5**, containing only 3 chiral centers connected *via* the amide group. It is supposed that formation of helical supramolecular aggregates by asymmetrical disks **4** and **5** is induced by urea-urea hydrogen bonding, followed by amide-amide intermolecular hydrogen bonding.

The applied synthetic method enables us to form asymmetrical disks **4** and **5** provided with two different hydrogen bonding groups. In the future also discotics containing different peripheral groups (e.g. hydrophobic and hydrophilic [16,19]) can be synthesized by this method, or discotics containing a "single tertiary handle" [19] or polymerizable groups. The concept of selective amide-amide and urea-urea stacking might prove useful in ordering these handles or functionalities.

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