From Molecular Ribbons to a Molecular Fabric

Mark Mascal,*[a] Jens Hansen,[a] Philip S. Fallon,[a] Alexander J. Blake,[a] Brigid R. Heywood,[b] Madeleine H. Moore,[c] and Johan P. Turkenburg[c]

Abstract: Ion-pair reinforced, hydrogen-bonded molecular ribbons are knitted together through ammonium carboxylate salt bridges into undulating sheets wherein each component participates in three ion-pairing interactions and up to twelve hydrogen bonds.

Keywords: crystal engineering · hydrogen bonds · ion pairs · self-assembly · solid-state structures

Introduction

'Crystal engineering' has in recent times become a byword of molecular science, and attempts are being made to deconvolute the variables which orchestrate the crystallization process and thereby formulate an algorithmic approach to the design of solids.[1] Despite this, relatively few molecules or systems of molecules crystallize in an entirely predictable way, and the best prospects for achieving a preconceived, higher order structural feature in a solid is to purpose–design components which present functional groups with powerful directing influences, such as hydrogen-bonding or metal–ligand relationships.

A good example of a self-organizing system which meets the above criterion is the hydrogen-bonding molecular ribbon first introduced by Lehn et al.[2] and Whitesides et al.[3] in 1990, and several applications of this dependable means of generating long-range order have since been described.[4] However, in most cases the mode of assembly has been effectively one-dimensional, with non-associated, independent ribbons making up the crystal lattice. To date, the only report of interrelationships between molecular ribbons has involved weak I···N bonds in *N*-cyanophenyl-*N'*-iodophenylmelamine or nonspecific coulombic forces and hydrogen bonds in (H^+)melamine barbiturate.[5]

[a] Dr. M. Mascal, Dr. J. Hansen, P. S. Fallon, Dr. A. J. Blake
Department of Chemistry, University of Nottingham
Nottingham NG7 2RD (UK)
Fax: (+44) 115-9513564
E-mail: mark.mascal@nottingham.ac.uk

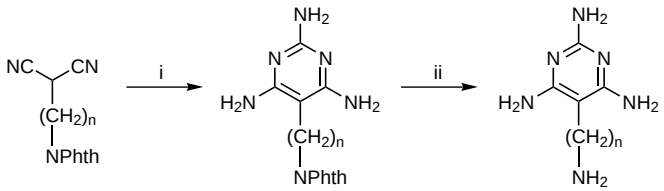
[b] Dr. B. R. Heywood
Department of Chemistry and Applied Chemistry
University of Salford
Salford M5 4WT (UK)

[c] Dr. M. H. Moore, Dr. J. P. Turkenburg
Department of Chemistry, University of York
Heslington, York YO1 5DD (UK)

We therefore became interested in extending the degree of control over this important solid-state motif into a second dimension[6] in a programmed fashion. This would be accomplished by installing electronically complementary functional groups into the tails of the components, which would cause the ribbons to converge. An acid–base ion pair seemed most suitable as it would provide a substantial interaction, while at the same time being flexible in terms of directionality and steric requirements. We now describe the modification of molecular ribbon components to include such functionality, and the faithful realization of the intended 'molecular program'.

Results and Discussion

A series of aminoalkyl-substituted pyrimidine-2,4,6-triamines (**1**) and carboxyalkyl 1,3,5-triazine-2,4,6-triones (**2**) were synthesized by modification of known methods[7] (Schemes 1 and 2). It was found that any combination of amine **1** with an

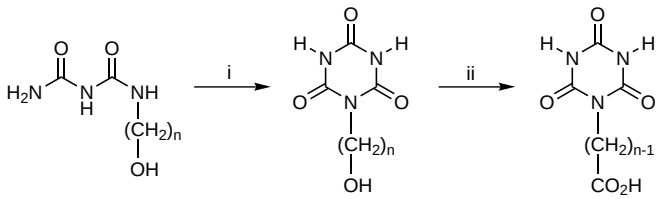


3 **4** **1**

Scheme 1. Reagents and conditions: i. $C(NH_2)_3^+Cl^-$, NaOEt, EtOH, reflux; ii. NH_2NH_2, EtOH, reflux, then NaOEt, reflux.

acid **2** in ethanol led to the immediate precipitation of 1:1 complexes (Scheme 3) which would only dissolve to an appreciable extent in polar aprotic solvents (DMF, DMSO) or water. Recrystallization of the complexes from water

  0947-6539/99/0501-0381 $ 17.50+.50/0



5 6 2

Scheme 2. Reagents and conditions: i. $(EtO)_2CO$, NaOEt, EtOH, reflux; ii. CrO_3/H_2SO_4, aqueous HOAc (**2a**); $NaIO_4/RuCl_3$, aqueous acetone (**2b**).

provided very thin plates which, in the case of **1a** + **2b** yielded to crystallographic analysis.

The structure of the **1a** + **2b** · $4H_2O$ complex is shown in Figure 1. As can be seen, pairs of ribbons related by a 180° *b* axis rotation are joined by salt bridges incorporating short hydrogen bonds between an ammonium H and carboxylate O atom (N ··· O 2.782(2) Å). The triply hydrogen-bonded faces of the ribbons are themselves alternately reinforced by ion pairing as a result of proton transfer from the triazinetrione to the pyrimidine ring.[8] These protons are located in difference Fourier maps, but also the effect of the opposing charges is manifested in the shorter N ··· O distances between the two rings on that side as compared to the other. The extended structure resembles an undulating sheet, where the criss-crossing interactions which constitute the fabric's 'weave' can be read off along the traditional ribbon axis (*c*) as repeating hydrogen-bond triplexes, and perpendicular thereto (*b*) as hydrogen-bond triplexes alternated by ammonium carboxylate bridges. The assembly can also be regarded as a honeycomb of interconnected, oblong **1a**$_3$**2b**$_3$ cyclic hexamers, where some comparison to the graphitic network between cyanuric acid and melamine can be drawn.[9] Each sheet is also associated with those directly above and below it through a second ammonium – carboxylate contact (N ··· O 2.780(2) Å) along an *a* glide (Figure 2), which renders the assembly continuous (i.e. three-dimensional). The three strong, linear

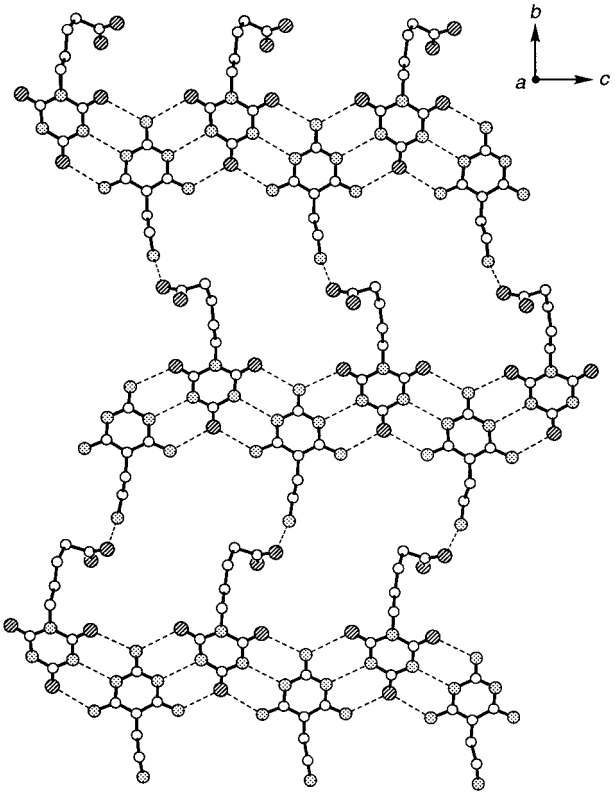


Figure 1. View of the **1a** + **2b** sheet with hydrogen atoms and water molecules omitted for clarity. The crystallographic axes are as shown.

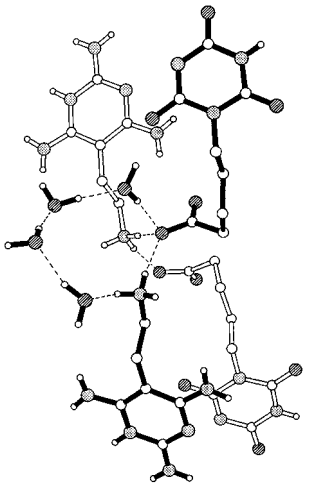
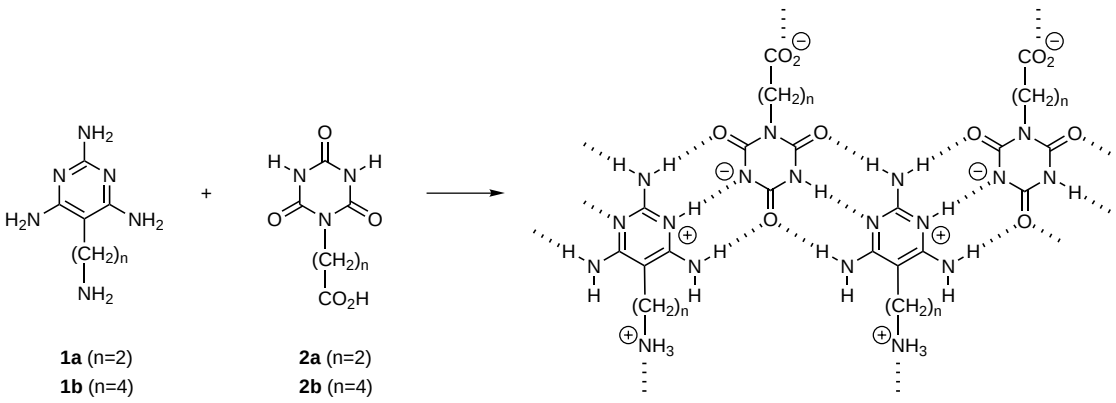


Figure 2. Detail from the **1a** + **2b** crystal structure showing the relationship of one sheet (filled bonds) to the one directly underneath it (unfilled bonds) as well as the water bridge between the opposing ribbons. Not shown are hydrogen bonds from the free triazinetrione oxygen sites to water molecules (one each) and the hydrogen atoms on carbon.



1a (n=2) **2a** (n=2)
1b (n=4) **2b** (n=4)

Scheme 3.

0947-6539/99/0501-0382 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 1

hydrogen bonds[10] to one of the carboxylate oxygen atoms represent an unusual trifurcation of electron density from a formally sp^2 hybridized centre.[11, 12] Finally, the bridging ion pairs are themselves bridged by a string of water molecules which together describe a six-membered, hydrogen-bonding ring (Figure 2). The four unique H_2O molecules assemble a continuous, highly twisted chain which weaves through the lattice and hydrogen bonds at every O atom with at least one component of the molecular complex.

Conclusion

This work demonstrates the programmability of hydrogen-bond triplex/ion-pair hybrid systems and their potential for engineering molecular solids for proliferation in set dimensions. The molecular ribbon is put in a new context as part of a two-dimensional assembly by the programmed coupling of ionics with hydrogen bonding. Further applications of this effective combination of design principles are under investigation and will be reported in due course.

Experimental Section

***N*-(3,3-Dicyanopropyl)phthalimide (3a)**: To a stirred suspension of sodium hydride (60% in oil, 0.880 g, 22.0 mmol) in DMSO (20 mL) was added a solution of malononitrile (2.64 g, 40.0 mmol) in DMSO (5 mL) with cooling. After addition was complete, the mixture was stirred for 10 min, the temperature raised to 80 °C and *N*-(2-bromoethyl)phthalimide (5.08 g, 20.0 mmol) was added in one portion. The mixture was stirred for 3 h at 90 °C before being allowed to cool. The reaction mixture was poured into water (50 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic extract was washed with water (3 × 100 mL), saturated aqueous sodium chloride (2 × 100 mL), dried over magnesium sulfate and the solvent removed to give an orange oil. Chromatography on silica gave **3a** (2.11 g, 44%) as a white solid, m.p. 109–110 °C; IR($CHCl_3$): $\tilde{\nu}$ = 2912, 2260 (C≡N), 1777 (C=O), 1715 (C=O), 1615, 1400, 1355, 1131 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (2H, q, *J* 6.5, 2′-H), 3.96-3.99 (3H, m, 1′-H and 3′-H), 7.76 (2H, m, Ar*H*), 7.87 (2H, m, Ar*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 20.8 (C-3′), 30.0 (C-2′), 34.4 (C-1′), 112.1 (CN), 123.6 (Ar), 131.5 (Ar), 134.4 (Ar), 168.1 (C=O); MS (EI): *m/z* (%): 239 ([M^+], 21), 174 (9), 161 (32), 160 (100), 148, (6), 133 (8), 130 (8), 105 (10), 104 (11), 77 (10), 76 (15); HRMS (EI) $C_{13}H_9N_3O_2$: calcd 239.0695; found 239.0697 ([M^+]).

***N*-(5,5-Dicyanopentyl)phthalimide (3b)**: Malononitrile (4.78 g, 72.4 mmol) in DMSO (10 mL), sodium hydride (60% in oil, 1.59 g, 39.8 mmol) in DMSO (35 mL) and *N*-(4-bromobutyl)phthalimide (10.2 g, 36.2 mmol) were allowed to react under conditions identical to those described for the preparation of **3a** to give **3b** (6.88 g, 71%) as a white solid, m.p. 137–138 °C; IR($CHCl_3$): $\tilde{\nu}$ = 2946, 2868, 2259 (C≡N), 1771 (C=O), 1715 (C=O), 1616, 1461, 1357, 1128, 995 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.67 (2H, m, 3′-H), 1.79 (2H, quintet, *J* 7.1, 2′-H), 2.11 (2H, q, *J* 7.6, 4′-H), 3.72 (2H, t, *J* 6.9, 1′-H), 3.81 (1H, t, *J* 6.9, 5′-H), 7.72 (2H, m, Ar*H*), 7.83 (2H, m, Ar*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 22.4 (C-5′), 23.6 (C-3′), 27.2 (C-2′), 30.0 (C-4′), 36.7 (C-1′), 112.4 (CN), 123.2 (Ar), 131.8 (Ar), 134.0 (Ar), 168.3 (C=O); MS (EI): *m/z* (%): 267 ([M^+], 2%), 240 (6), 202 (10), 160 ($PthCH_2^+$·, 100), 104 (6), 77 (8), 76 (7); elemental analysis calcd for $C_{15}H_{13}N_3O_2$: C 67.4, H 4.9, N 15.7; found C 67.2, H 4.9, N 15.6.

5-(2-Phthalimidoethyl)-2,4,6-triaminopyrimidine (4a): To a stirred solution of sodium ethoxide (782 mg, 11.5 mmol) in ethanol (12 mL) was added guanidine hydrochloride (742 mg, 7.77 mmol). The mixture was stirred for 5 min and filtered to remove the precipitated sodium chloride. To the resulting solution was added *N*-(3,3-dicyanopropyl)phthalimide **3a** (1.67 g, 6.98 mmol) and the mixture was heated at reflux for 3 h. The reaction was allowed to cool, filtered, the residue washed with cold ethanol and dried to give **4a** (1.62 g, 78%) as a yellow powder, m.p. 255–257 °C; IR(KBr): $\tilde{\nu}$ = 3386, 2940, 1765 (C=O), 1703 (C=O), 1620, 1577, 1450, 1402, 1362, 1086, 794, 722 cm^{-1}; ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 2.58 (2H, t, *J* 7.0, 1′-H), 3.59 (2H, t, *J* 7.0, 2′-H), 5.41 (2H, s, 2-NH_2), 5.58 (4H, s, 4-NH_2 and 6-NH_2), 7.82 (4H, m, Ar*H*); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 22.2 (C-1′), 35.9 (C-2′), 82.1 (C-5), 123.0 (Ar), 131.7 (Ar), 134.4 (Ar), 160.5 (C-2), 162.2 (C-4 and C-6), 168.2 (C=O); MS (EI): *m/z* (%): 298 ([M^+], 1), 160 ($PthCH_2^+$·, 4), 150 (4), 138 (TAP-CH_2^+·, 100), 121 (14), 104 (12), 96 (25), 76 (17); HRMS (EI) $C_{14}H_{14}N_6O_2$: calcd 298.1178; found 298.1187 ([M^+]).

5-(4-Phthalimidobutyl)-2,4,6-triaminopyrimidine (4b): Guanidine hydrochloride (2.63 g, 27.5 mmol), sodium ethoxide (2.81 g, 41.3 mmol) in ethanol (25 mL) and *N*-(5,5-dicyanopentyl)phthalimide **3b** (6.68 g, 25.0 mmol) were allowed to reated under conditions identical to those described for the preparation of **4a** to give **4b** (6.21 g, 76%) as a yellow powder, m.p. 230–232 °C; IR(KBr): $\tilde{\nu}$ = 3434, 3382, 3181, 2940, 2882, 1768 (C=O), 1708 (C=O), 1616, 1572, 1450, 1438, 1400, 718 cm^{-1}; ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.28 (2H, m, 2′-H), 1.63 (2H, m, 3′-H), 2.16 (2H, t, *J* 7.7, 1′-H), 3.56 (2H, t, *J* 6.8, 4′-H), 5.12 (2H, s, 2-NH_2), 5.41 (4H, s, 4-NH_2 and 6-NH_2), 7.83 (4H, m, Ar*H*); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 22.7 (C-1′), 25.4 (C-2′), 28.1 (C-3′), 37.5 (C-4′), 85.5 (C-5), 122.9 (Ar), 131.6 (Ar), 134.3 (Ar), 160.6 (C-2), 161.9 (C-4 and C-6), 168.0 (C=O); MS (EI): *m/z* (%): 327 (8), 326 ([M^+], 17), 138 (100); HRMS (EI) $C_{16}H_{18}N_6O_2$: calcd 326.1491; found 326.1503 ([M^+]).

5-(2-Aminoethyl)-2,4,6-triaminopyrimidine (1a): To a stirred suspension of 5-(2-phthalimidoethyl)-2,4,6-triaminopyrimidine **4a** (894 mg, 3.00 mmol) in ethanol (30 mL) was added hydrazine hydrate (0.400 mL) and the mixture heated at reflux for 24 h. The reaction was allowed to cool to room temperature, sodium ethoxide (204 mg, 3.00 mmol) in ethanol (8 mL) was added and the mixture heated at reflux for an additional 30 min. The reaction was cooled to 0 °C, filtered through Celite and the filtrate evaporated to dryness. The residual yellow solid was recrystallized from water to give **1a** (297 mg, 59%) as white needles, m.p. 191–192 °C; IR(KBr): $\tilde{\nu}$ = 3377, 3182, 2932, 1625, 1582, 1437, 1030, 813 cm^{-1}; ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 2.23 (2H, t, *J* 7.2, 1′-H), 2.49 (2H, m, 2′-H), 3.33 (2H, br s, 2′-NH_2), 5.27 (2H, s, 2-NH_2), 5.58 (4H, s, 4-NH_2 and 6-NH_2); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 28.2 (C-1′), 40.7 (C-2′), 84.0 (C-5), 160.7 (C-2), 162.4 (C-4 and C-6); MS (EI): *m/z* (%): 168 ([M^+], 14), 151 (7), 150 (10), 149 (9), 139 (63), 138 (100), 121 (14), 96 (17); HRMS (EI) $C_6H_{12}N_6$: calcd 168.1124; found 168.1120 ([M^+]).

5-(4-Aminobutyl)-2,4,6-triaminopyrimidine (1b): 5-(4-Phthalimidobutyl)-2,4,6-triaminopyrimidine **4b** (4.89 g, 15.0 mmol) in ethanol (150 mL), hydrazine hydrate (1.60 mL) and sodium ethoxide (1.02 g, 15.0 mmol) in ethanol (15 mL) were allowed to react under conditions identical to those described for the preparation of **1a** to give **1b** (2.79 g, 95%) as yellow needles, m.p. 119–121 °C; IR(KBr): $\tilde{\nu}$ = 3479, 3399, 3102, 2939, 2869, 1623, 1584, 1436, 810 cm^{-1}; ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 1.28-1.35 (4H, m, 2′-H and 3′-H), 2.12 (2H, br s, 1′-H), 2.48 (2H, m, 4′-H), 2.58 (2H, br s, 4′-NH_2), 5.31 (2H, s, 2-NH_2), 5.60 (4H, s, 4-NH_2 and 6-NH_2); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 22.9 (C-1′), 25.3 (C-2′), 32.7 (C-3′), 41.7 (C-4′), 85.9 (C-5), 160.5 (C-2), 162.0 (C-4 and C-6); MS (EI): *m/z* (%): 196 ([M^+], 18), 180 (5), 153 (9), 152 (9), 138 (100), 126 (12), 125 (12), 96 (7); HRMS (EI) $C_8H_{16}N_6$: calcd 196.1437; found 196.1432 ([M^+]).

1-(3-Hydroxypropyl)biuret (5a): 1-Nitrobiuret (24.6 g, 166 mmol) was suspended in water (150 mL) and 3-amino-1-propanol (12.5 g, 166 mmol) was added. The mixture was allowed to stand for 1 h with occasional swirling and then heated at reflux for 1 h. The solution was then cooled on ice and filtered to remove a small amount of insoluble material before being concentrated to give the crude product as a white solid. Recrystallization from ethanol gave **5a** (15.7 g, 59%) as a white solid, m.p. 118–121 °C; IR(KBr): $\tilde{\nu}$ = 3460, 3408, 3287, 3251, 2962, 2923, 1716 (C=O), 1686 (C=O), 1650, 1605, 1566, 1499, 1337, 1304, 1268, 1237, 1056, 660, 580 cm^{-1}; ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 1.53 (2H, quintet, *J* 6.5, 2′-H), 3.12 (2H, q, *J* 6.4, 1′-H), 3.39 (2H, q, *J* 5.5, 3′-H), 4.48 (1H, t, *J* 5.2, OH), 6.71 (2H, s, 5-H), 7.48 (1H, br s, 1-H), 8.53 (1H, s, 3-H); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 32.6 (C-2′), 36.1 (C-1′), 58.4 (C-3′), 154.6, 155.7 (C-2 and C-4); MS (EI): *m/z* (%): 161 ([M^+], 0.3), 130 ([$M - CH_2OH$], 2), 116 (8), 101 (50), 88 (13), 60 (45), 56 (50), 44 (84), 43 (100); elemental analysis calcd for $C_5H_{11}N_3O_3$: C 37.3, H 6.9, N 26.1; found C 37.0, H 7.1, N 26.1.

1-(5-Hydroxypentyl)biuret (5b): 1-Nitrobiuret (22.2 g, 150 mmol) and 5-amino-1-pentanol (15.5 g, 150 mmol) were allowed to react under

conditions identical to those described for the preparation of **5a** to give **5b** (15.0 g, 53%) as a white solid, m.p. 116–118 °C; IR(KBr): $\tilde{\nu}$ = 3404, 3320, 2939, 2864, 1701 (C=O), 1679 (C=O), 1546, 1440, 1243, 1058, 661 cm^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.26 (2H, m, 3′-H), 1.36-1.43 (4H, m, 2′-H and 4′-H), 3.06 (2H, q, *J* 6.5, 1′-H), 3.36 (2H, q, *J* 5.8, 5′-H), 4.34 (1H, t, *J* 4.5, OH), 6.71 (2H, s, 5-H), 7.44 (1H, br s, 1-H), 8.49 (1H, s, 3-H); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 22.9 (C-3′), 29.3 (C-2′), 32.2 (C-4′), 38.8 (C-1′), 60.6 (C-5′), 154.4, 155.6 (C-2 and C-4); MS (EI): *m/z* (%): 190 ([*M* + 1], 3), 189 ([*M*$^+$], 4), 156 (7), 145 (10), 130 (21), 116 (93), 102 (43), 99 (78), 87 (25), 70 (59), 44 (100); elemental analysis calcd for $C_7H_{15}N_3O_3$: C 44.4, H 8.0, N 22.2; found C 44.1, H 8.3, N 22.5.

1-(3-Hydroxypropyl)-1,3,5-triazine-2,4,6-trione (**6a**): A solution of sodium ethoxide was prepared from sodium metal (138 mg, 6.0 mmol) and absolute ethanol (6 mL). Diethyl carbonate (472 mg, 4.00 mmol) was added with stirring, followed by 1-(3-hydroxypropyl)biuret (**5a**) (322 mg, 2.00 mmol) and the mixture was heated at reflux for 2 h, during which the sodium salt of the product precipitated from solution. The mixture was allowed to cool to room temperature, filtered and the precipitate washed with cold 1:1 ethanol-ether. The salt was then dissolved in the minimum volume of water and the solution was carefully neutralized by the addition of 1M sulfuric acid whereupon precipitation occurred. The product was collected on a filter, washed and dried under vacuum to give **6a** (225 mg, 60%) as a white solid, m.p. 220–223 °C; IR(KBr): $\tilde{\nu}$ = 3500, 3059, 2807, 1755 (C=O), 1696 (C=O), 1676 (C=O), 1481, 1450, 1415, 1124, 1030, 937, 862, 839, 758 cm^{-1}; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 1.64 (2H, quintet, *J* 6.7, 2′-H), 3.40 (2H, br s, 3′-H), 3.67 (2H, t, *J* 7.2, 1′-H), 4.45 (1H, br s, OH), 11.13 (2H, s, NH); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 30.7 (C-2′), 38.5 (C-1′), 58.7 (C-3′), 148.7 (C-4), 149.9 (C-2 and C-6); MS (EI): *m/z* (%): 187 ([*M*$^+$], 2), 169 ([*M* – H$_2$O], 15), 157 (86), 143 (28), 142 (14), 130 (100), 70 (30), 56 (37); elemental analysis calcd for $C_6H_9N_3O_4$: calcd C 38.5, H 4.8, N 22.5; found: C 38.4, H 4.9, N 22.7.

1-(5-Hydroxypentyl)-1,3,5-triazine-2,4,6-trione (**6b**): Sodium ethoxide (7.5 mmol) in absolute ethanol (7.5 mL), diethyl carbonate (590 mg, 5.00 mmol) and 1-(5-hydroxypentyl)biuret **5b** (473 mg, 2.50 mmol) were allowed to react under conditions identical to those described for the preparation of **6a** to give **6b** (425 mg, 79%) as a white solid, m.p. 182–183 °C; IR(KBr): $\tilde{\nu}$ = 3486, 3202, 3067, 2936, 2816, 1746 (C=O), 1689 (C=O), 1485, 1454, 1418, 1155, 1067, 761, 542 cm^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.24 (2H, m, 3′-H), 1.40 (2H, quintet, *J* 7.0, 2′-H), 1.48 (2H, quintet, *J* 7.5, 4′-H), 3.35 (2H, t, *J* 6.4, 5′-H), 3.60 (2H, t, *J* 7.3, 1′-H), 4.31 (1H, br s, OH), 11.36 (2H, s, NH); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 22.7 (C-3′), 27.3 (C-2′), 32.2 (C-4′), 40.5 (C-1′), 60.5 (C-5′), 148.7 (C-4), 149.9 (C-2 and C-6); MS (EI): *m/z* (%): 185 ([*M* – CH$_2$O], 15), 155 (10), 143 (7), 142 (8), 130 (100), 68 (64), 56 (27); elemental analysis calcd for $C_8H_{13}N_3O_4$: C 44.6, H 6.1, N 19.5; found C 44.4, H 6.3, N 19.7.

1-(2-Carboxyethyl)-1,3,5-triazine-2,4,6-trione (**2a**): Concentrated sulfuric acid (1 mL) was added to water (2 mL) and the solution diluted to 10 mL with acetic acid. To this was added 1-(3-hydroxypropyl)-1,3,5-triazine-2,4,6-trione **6a** (1.87 g, 10.0 mmol) with stirring. A chromic acid solution (made by dissolving chromium trioxide (2.5 g, 25 mmol) in water (2.5 mL) and diluting to 10 mL with acetic acid) was added dropwise over 1 h and the mixture was left to stand overnight. The solution was then heated at reflux for 1 h and allowed to cool to room temperature whereupon precipitation occurred. The green precipitate was collected on a filter and recrystallized four times from water to yield **2a** (1.11 g, 55%) as a very pale green solid, m.p. 266–267 °C; IR(KBr): $\tilde{\nu}$ = 3419, 3235, 2796, 1757 (C=O), 1723 (C=O), 1693 (C = O), 1470, 1399, 1192, 1171, 1122, 1038, 805, 762, 552, 516 cm^{-1}; ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 1.56 (2H, t, *J* 7.0, 2′-H), 2.92 (2H, t, *J* 7.0, 1′-H), 10.52 (2H, br s, NH), 11.44 (1H, br. s, OH); ^{13}C NMR (67.8 MHz, [D$_6$]DMSO): δ = 32.0 (C-2′), 36.4 (C-1′), 148.7 (C-4), 149.7 (C-2 and C-6), 172.3 (C-3′); MS (EI): *m/z* (%): 183 ([*M* – H$_2$O], 12), 155 (100), 142 (16), 130 (11), 70 (26), 69 (24), 56 (51); elemental analysis calcd for $C_6H_7N_3O_5$: C 35.8, H 3.5, N 20.9; found: C 35.6, H 3.6, N 20.9.

1-(4-Carboxybutyl)-1,3,5-triazine-2,4,6-trione (**2b**): To a stirred solution of 1-(5-hydroxypentyl)-1,3,5-triazine-2,4,6-trione **6b** (0.25 g, 1.2 mmol) in 70% aqueous acetone (10 mL) was added sodium periodate (1.2 g, 5.6 mmol) and ruthenium trichloride (1.0 mg). The reaction mixture was stirred overnight at room temperature before being concentrated and recrystallized from water to give **2b** (0.17 g, 64%) as a pale grey solid, m.p. 239–242 °C; IR(KBr): $\tilde{\nu}$ = 3441, 3214, 3087, 2961, 1768 (C=O), 1752 (C=O), 1688 (C=O), 1468, 1420, 1407, 1376, 1219, 1052, 794, 762, 553 cm^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.45–1.50 (4H, m, 2′-H and 3′-H), 2.20 (2H, t, *J* 6.8, 4′-H), 3.61 (2H, t, *J* 6.5, 1′-H), 11.51 (2H, br s, NH); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 21.8 (C-3′), 27.0 (C-2′), 33.3 (C-4′), 40.2 (C-1′), 148.7 (C-4), 150.0 (C-2 and C-6), 174.4 (C-5′); MS (EI): *m/z* (%): 211 ([*M* – H$_2$O], 49), 193 (5), 183 (90), 170 (56), 155 (24), 142 (40), 130 (65), 54 (100); elemental analysis calcd for $C_8H_{11}N_3O_5$: C 41.9, H 4.8, N 18.3; found C 41.7, H 4.9, N 18.1.

Crystal data for the 1a + 2b · 4H$_2$O complex: $C_{14}H_{31}N_9O_9$, M_r = 469.48, colorless crystal 0.80 × 0.50 × 0.05 mm, monoclinic, a = 7.849(1), b = 30.790(1), c = 9.634(1) Å, β = 108.52(10)°, U = 2207.7(4) Å^3, T = 293(2) K, space group $P2_1/a$ (No. 14), Z = 4, ρ_{calcd} = 1.413 g cm^{-3}, λ = 0.87 Å, μ = 0.118 mm^{-1}, 11815 reflections measured, 2303 unique (R_{int} = 0.056), final $R_1[F_O \geq 4\sigma(F_O)]$ = 0.0447, wR_2 (all data) = 0.119 for 315 refined parameters. Intensity data were collected using a 30 cm MAR imaging plate mounted on beamline PX 9.6 of the Synchrotron Radiation Source at the CLRC Daresbury Laboratory, and processed using DENZO and SCALEPACK (Z. Otwinowski, W. Minor, *Methods in Enzymology* **1997**, *276*, 307). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102530. Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336033; e-mail: deposit@ ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the ICI Strategic Research Fund, EPSRC and BBSRC.

[1] Review: G. R. Desiraju, *Chem. Commun.* **1997**, 1475, and references therein.
[2] J.-M. Lehn, M. Mascal, A. DeCian, J. Fischer, *J. Chem. Soc. Chem. Commun.* **1990**, 479.
[3] J. A. Zerkowski, C. T. Seto, D. A. Wierda, G. M. Whitesides, *J. Am. Chem. Soc.* **1990**, *112*, 9025.
[4] For some examples of how various research groups have made use of the hydrogen-bonding ribbon motif, see: a) V. Marchi-Artzner, L. Jullien, T. Gulik-Krzywicki, J.-M. Lehn, *Chem. Commun.* **1997**, *117*; b) H. Koyano, P. Bissel, Y. Yoshihara, K. Ariga, T. Kunitake, *Chem. Eur. J.* **1997**, *3*, 1077; c) W. T. S. Huck, R. Hulst, P. Timmerman, F. C. J. M. van Veggel, D. N. Reinhoudt, *Angew. Chem.* **1997**, *109*, 1046; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1006; d) Y. Ren, B. Zhao, X. Chai, A. Lu, S. Chen, Y. Cao, W. Yang, R. Lu, J. Duo, Y. Jiang, T. Li, *Thin Solid Films* **1997**, *293*, 170; e) T. M. Bohanon, S. Denziner, R. Fink, W. Paulus, H. Ringsdorf, M. Weck, *Angew. Chem.* **1995**, *107*, 102; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 58; f) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37; g) K. Hanabusa, Y. Miki, Y. Taguchi, T. Koyama, H. Shirai, *J. Chem. Soc. Chem. Commun.* **1993**, 1382.
[5] J. A. Zerkowski, J. C. MacDonald, G. M. Whitesides, *Chem. Mater.* **1994**, *6*, 1250.
[6] The application of hydrogen bonding to the generation of other two-dimensional assemblies has been reviewed: D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229.
[7] D. A. Dunnigan, W. J. Close, *J. Am. Chem. Soc.* **1953**, *75*, 3615; W. J. Close, *J. Am. Chem. Soc*. **1953**, *75*, 3617; P. B. Russell, G. H. Hitchings, *J. Am. Chem. Soc.* **1952**, *74*, 3443.
[8] M. Mascal, P. S. Fallon, A. S. Batsanov, B. R. Heywood, S. Champ, M. Colclough, *J. Chem. Soc. Chem. Commun.* **1995**, 805.
[9] C. T. Seto, G. M. Whitesides, *J. Am. Chem. Soc.* **1990**, *112*, 6409.
[10] H ··· O distances < 2.0 Å, X – H ··· O angles > 170°.
[11] The low incidence of trifurcated C=O hydrogen-bond acceptors has been determined by use of the Cambridge Structural Database: C. M. Bird, PhD Thesis, University of Cambridge, **1995**.
[12] The Cambridge Structural Database: F. H. Allen, O. Kennard, *Chemical Design Automation News* **1993**, *8*, 31.

Received: October 26, 1998 [F1414]

  0947-6539/99/0501-0384 $ 17.50+.50/0