# New supramolecular arrays based on interactions between carboxylate and urea groups: solid-state and solution behavior

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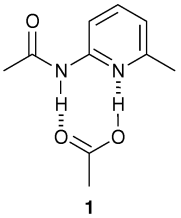
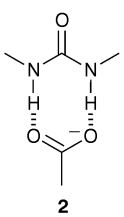
The urea–carboxylate interaction is introduced as a potentially general motif for the control of solid-state packing patterns. We show that simple phenylurea carboxylate derivatives can form extended hydrogen-bonded ribbons in the crystal in which the zig-zag shape of the aggregate is controlled by the relative orientation of the two substituents about the phenyl core. We also show that an alternative type of aggregation may occur in solution involving the formation of cyclic aggregates. Again, the size and stability of the aggregate is dependent on the substitution pattern of the monomer.

In recent years there has been intense interest in the design of ordered solids.[1] The controlled alignment of similar (homoaggregates) or different (heteroaggregates) molecular components in the solid state can lead to novel materials with interesting properties. The power of molecular design in the preparation of these structures lies in its ability to fine tune solid-state properties by subtle modification of the shape and relative distances of the component pieces. A key requirement of this strategy is that the primary intermolecular interactions that define the crystal packing pattern be sufficiently robust to withstand such changes in the size, shape and orientation of the individual subunits without loss of overall morphology. A variety of approaches have been taken to impose strong, directional and, where possible, predictable interactions between components in a solid-state structure. Two of the most successful strategies have included the use of metal–ligand[2] or complementary hydrogen-bonding interactions[3] to control both the stability and orientation of intermolecular packing in the crystal.

We have previously reported that the bidentate hydrogen-bonding interaction between carboxylic acid and acylaminopyridine groups (as in **1**) can be a versatile motif in crystal engineering.[4] In particular, a series of aliphatic dicarboxylic acids and bis-acylaminopyridine derivatives were shown to form polymeric hydrogen-bonded ribbon structures that persisted despite major changes in the identity of the spacer groups.[5] Furthermore, the relative angle between the components in the cocrystal could be controlled by varying the separation of the hydrogen-bonding groups in a predictable manner. Motif **1** is limited however by the weakness of its hydrogen bonds between two neutral functional groups.[6] This feature is manifested in solution by the absence of any detectable interaction between carboxylic acids and acylaminopyridine derivatives in polar solvents.[7] A significant improvement in the strength of bidentate hydrogen bonds can be achieved by using charged rather than neutral partners. For example, urea and thiourea groups can function as double hydrogen-bond donors to form a bidentate interaction with carboxylate salts, as in **2**. These complexes show appreciable stability in such polar organic solvents as $(CH_3)_2SO$ (DMSO) and methanol.[7]



**1**



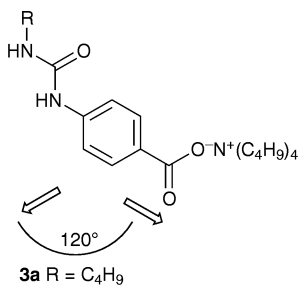
**2**

In the present paper we extend the development of hydrogen-bonded ribbons to include components containing urea and carboxylate groups. We show that these derivatives form extended ribbon structures in which the relative orientation of the components is controlled by their substitution pattern.

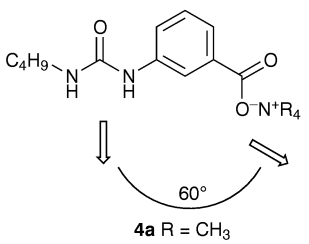
The target tetrabutyl- and tetramethyl-ammonium salts of the *N*-butylureabenzoates **3a** and **4a** were synthesized by treating 4-aminobenzoic acid and 3-aminobenzoic acid, respectively, with n-butylisocyanate followed by reaction with a stoichiometric amount of the tetraalkylammonium hydroxide in methanol.

Crystals of the tetrabutylammonium salt of **3a** were grown from DMSO at room temperature. The X-ray crystal structure shows (Fig. 1A) that bidentate hydrogen bonds (N···O, 2.76 and 2.93 Å) between the carboxylate and urea groups are the primary organizing interaction in the solid state. A linear ribbon structure is formed with an approximately planar orientation of the phenyl, carboxylate and urea groups. The relative orientation of the components is controlled by the angle from which the two hydrogen-bonding groups project from the central benzene ring. In **3a** this angle is ≈120° and the result is an open zig-zag ribbon arrangement.

The tetrabutylammonium counter ions are positioned directly above (or below) the carboxylate–urea unit with ammonium-N to carboxylate-O distances of 4.19–4.57 Å. The result is a layered arrangement in which the tetrabutylammonium ions alternate with the hydrogen bonding ribbons (Fig. 1B). The butyl chains on the urea groups project above (or below) the plane of each hydrogen bonded ribbon and pack closely with the butyl groups of the cation.




**3a** R = $C_4H_9$
**3b** R = $C_{10}H_{21}$




**4a** R = $CH_3$
**4b** R = $C_4H_9$

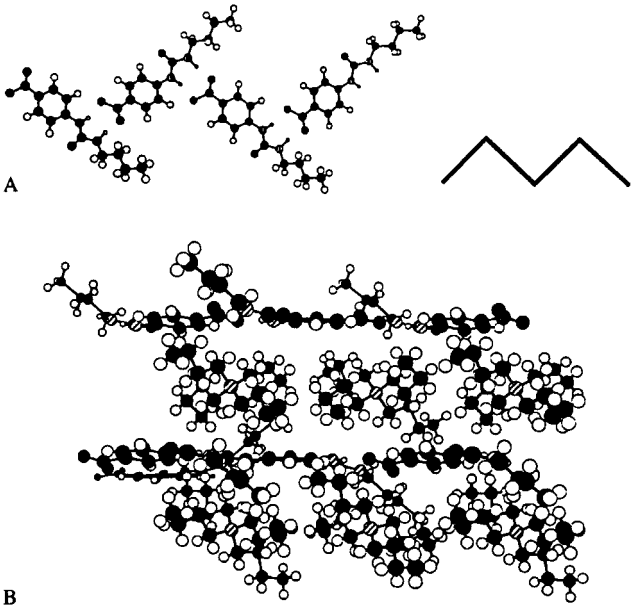



Fig. 1 Crystal structure of **3a** showing: A, individual hydrogen-bonded ribbons; B, layered arrangement of ribbons and counter ions

A very similar solid state structure is seen in **4a** (Fig. 2) with bidentate hydrogen bonds (N···O, 2.87 and 3.00 Å) formed between the urea and carboxylate groups. In this case, however, the substituents project from the phenyl core with a more acute angle of $\approx 60°$ leading to a more compact zig-zag orientation of the hydrogen-bonded components. Another interesting feature is the presence of a water molecule bridging between two carboxylate groups on adjacent subunits. Presumably the water plays an important role in reducing the unfavorable Coulombic interaction between the more closely spaced carboxylate groups (O···O, 4.4 Å in **4a** and 7.25 Å in **3a**). A similar multilayer structure is seen with alternating tetramethylammonium counter ions and hydrogen-bonded ribbons (Fig. 2B).

The urea–carboxylate derivatives **3a** and **4a** form extended hydrogen-bonded polymers in the solid state. However, the 1,4- and 1,3-disubstituted phenyl species could also form hydrogen-bonded aggregates *via* an alternative mode of interaction, namely cyclization. We had previously shown that acylaminopyridine and carboxylic acid derivatives could form extended[4] or cyclic aggregates[3,9] (of type **1**) depending on the conditions and the nature of the interacting components. Similarly, bis-urea and bis-carboxylates can form cyclic 1 : 1 hydrogen-bonded complexes (of type **2**) or melamine and barbiturate derivatives can form cylcic 3 + 3 rosettes in solution.[10] For **3** and **4** the angle between the substituents should control the type of cyclic aggregate formed (Fig. 3). For **3** (120° angle), molecular modeling[11] suggested that both cyclic hexamers and cyclic pentamers (*e.g.* **5**) can be formed from, respectively, the planar and non-planar disposition of the hydrogen-bonding groups. However, with **4** (60° angle) cyclic trimers (*e.g.* **6**) appear geometrically favored with no apparent distortion of the bidentate hydrogen bonds. In solution, cyclization of this type may be favored since $2n$ hydrogen bonds are formed from $n$ associating particles compared to only $(2n - 2)$ for a linear type of aggregation.

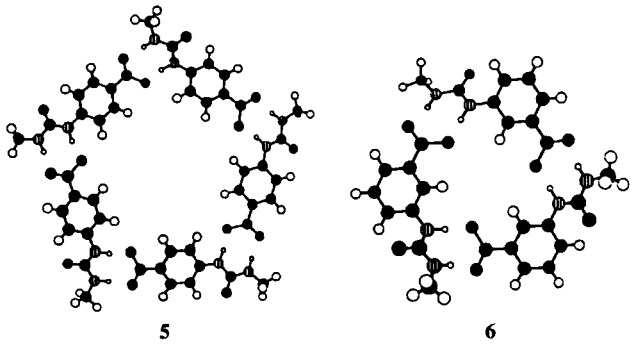



**Fig. 3** Ball and stick representations of the hypothetical cyclic aggregates that can be formed by **3** and **4**[11]

In order to investigate the solution aggregation behavior of **3a** and **4a** we have employed NMR dilution and vapor pressure osmometry techniques. Ideally, a plot of NMR chemical shift change *vs.* log[conc] should give a sigmoidal curve progressing from monomer at low concentration to oligomer at high concentration. The shape of the dilution curve and, in particular, the slope at the inflection point corresponds to the equilibrium constant for aggregation. $^1$H NMR dilution experiments were performed under four different solvent conditions; $CDCl_3$, $(CD_3)_2SO$–$CDCl_3$ (1 : 10), $(CD_3)_2SO$–$CDCl_3$ (1 : 5) and $(CD_3)_2SO$, over a concentration range 0.1–100 mM. In $CDCl_3$ there was almost no shift in the urea-NH resonances, suggesting very strong interaction. In the more polar solvent conditions the urea-NH resonances shifted downfield by 1.5–3.0 ppm as the concentration increased. However the shapes of the dilution curves of **3** and **4** are remarkably different despite their closely related structures (Fig. 4). In particular, while the NH chemical shift values are similar in dilute solution they differ by more than 1 ppm at higher concentra-

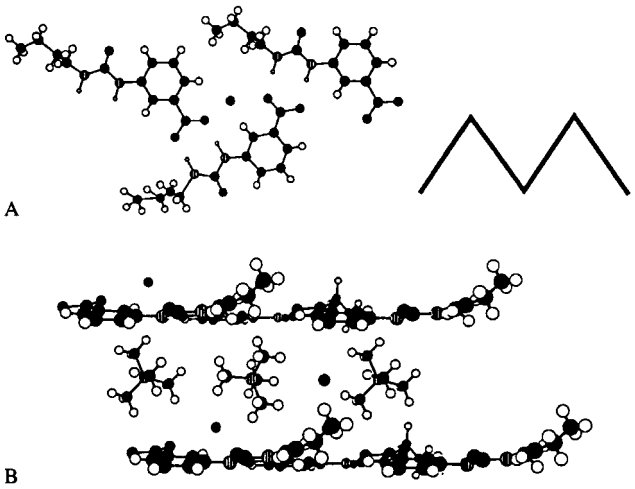



**Fig. 2** Crystal structure of **4a**[8] showing: A, individual hydrogen bonded ribbons; B, layered arrangement of ribbons and counter ions

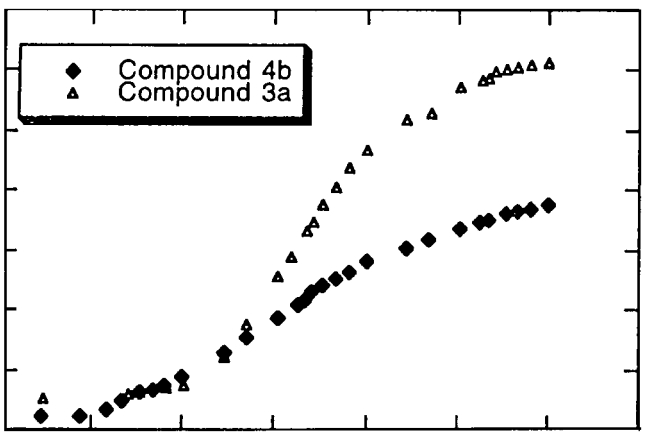



**Fig. 4** Plot of log[conc] *vs.* NMR chemical shift for aryl N-H in $(CD_3)_2SO$–$CDCl_3$ (1 : 5) for **3a** (△) and **4b** (◆)

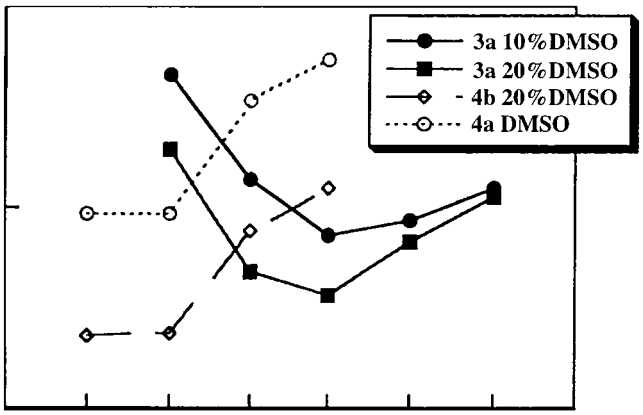



**Fig. 5** Plot of $\Sigma\chi^2$ *vs.* aggregation number *n* for **3** and **4** in different solvent systems

tion, suggesting a stronger hydrogen bonding interaction for **3** over **4** at 100 mM. These effects are probably not due to any differences in the basicity of the two carboxylates since $pK_a$ values of 7.9 and 7.6 were measured for **3a** and **4a**, respectively, in $(CH_3)_2SO$–$H_2O$ (3:1). The trimer model for the possible cyclic aggregate of **4** places carboxylate groups on adjacent subunits in close proximity and the resulting unfavorable Coulombic interaction may destabilize the aggregate while there is a lesser destabilization in the case of **4**.

We have used a modification of the Saunders and Hyne model[12,13] to analyze the two dilution curves. The analysis is based on the assumption that there are only two measurable species (monomer and the most stable oligomer) present in solution which are under fast exchange. We have developed a program to simulate the NMR dilution data to fit the Saunders and Hyne model using different aggregation numbers.[14] The goodness of the fit is measured by comparing the chi square value of different curve fits. The dilution data for **3a** fits best to the monomer–pentamer model (Fig. 5). The dilution behavior of **4** was found to be more complicated than **3a**, with a better fit to the monomer–dimer model in the majority of cases (Fig. 5). This analysis further supports the chemical shift data in suggesting that the trimeric aggregate of **4a** is less stable than the pentameric aggregate of **3a**. The primary cause of this difference may be coulombic repulsion as the calculated structures of cyclic complexes (Fig. 3) show carboxylate–carboxylate distances of 8.5 and 7.05 Å for the pentamer and trimer, respectively.

These interpretations were supported by vapor pressure osmometry (VPO)[15] experiments in chloroform using benzil as the standard. The experimental molecular weight obtained for **3b** at 40 °C is 2400 Da (1 Da $\approx 1.660 \times 10^{-27}$ kg) which is in between the molecular weight of a tetramer (2244) and a pentamer (2805 Da). The experimental molecular weight obtained for **4b** at 34 °C is 1050 Da which is closer to the theoretical molecular weight of a dimer (954 Da) compared to that of a trimer (1431 Da).

In summary, we have shown that urea carboxylate derivatives can form hydrogen-bonded ribbon structures in the solid state, in which the shape of the aggregate is controlled by the orientation of the two substituents. In solution an alternative interaction can occur potentially leading to cyclic structures. Preliminary evidence suggests substitution pattern also influences the size and stability of the aggregate in solution.

## Experimental

### 4-(3-Butylureido)benzoic acid

To a solution of 4-aminobenzoic acid (1 g, 7.29 mmol) in methylene chloride–THF (1 : 1) (70 mL) was added n-butylisocyanate (0.92 ml, 8.02 mmol) and the solution was stirred for 12 h. The precipitated product was suction filtered and washed with hydrochloric acid (1 M) and water. The white cake was then air dried to obtain the product. (1.08 g, 62.6%): m.p. 250° decomp.; $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 0.88 (t, $J$ = 7.1, 3H, $CH_3$), 1.20–1.50 (m, 4H, $CH_2$), 3.07 (m, 2H, urea $CH_2$), 6.26 (br, 1H, urea H), 7.46 (d, $J$ = 8.7, 2H, PhH), 7.78 (d, $J$ = 8.6 Hz, 2H, PhH), 8.79 (s, 1H, urea H); $^{13}$C NMR [75 MHz, $(CD_3)_2SO$] δ 13.7, 19.5, 31.7, 116.5, 122.7, 130.5, 144.9, 154.8, 167.1; MS (EI) *m/z* calcd for $C_{12}H_{16}N_2O_3$: 236.1160, found 236. Analysis: calcd for $C_{12}H_{16}N_2O_3$: C, 60.99; H, 6.83; N, 11.86. Found: C, 61.10; H, 6.87; N, 11.92%.

### Tetrabutylammonium 4-(3-butylureido)benzoate 3a

To a solution of 4-(3-butylureido)benzoic acid (0.75 g, 3.18 mmol) in methanol was added a 1M solution of tetrabutylammonium hydroxide in methanol (3.18 mL, 3.18 mmol). The solvent was evaporated and the product was dried under vacuum. The product was then washed with acetone and dried under vacuum to yield a white powder (1.5 g, 99.0%): m.p. 173–176°; $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 0.86–0.93 (m, 15H, alkyl and ammonium $CH_3$), 1.21–1.51 (m, 20H, alkyl and ammonium $CH_2$), 3.02–3.14 (m, 10H, urea and ammonium $CH_2$), 7.41 (d, $J$ = 8.4, 2H, PhH), 7.70 (d, $J$ = 8.4 Hz, 2H, PhH), 8.10 (br, 1H, urea H), 10.33 (br, urea H); $^{13}$C NMR [75 MHz, $(CD_3)_2SO$] δ 13.5, 13.9, 19.2, 19.8, 23.0, 32.2, 57.5, 115.6, 129.6, 131.4, 143.3, 156.4, 170.7; MS (FAB) *m/z* calcd for $C_{28}H_{51}N_3O_3$: 477.3930, found 477. Analysis: calcd for $C_{28}H_{51}N_3O_3 \cdot 0.5H_2O$: C, 69.09; H, 10.77; N, 8.63. Found: C, 69.24; H, 10.70; N, 8.60%.

### 4-(3-decylureido)benzoic acid

A three neck round bottom flask was charged with decylamine (2.6 mL, 12.7 mmol), dichloromethane (42 mL) and pyridine (4.15 mL). The mixture was cooled in an ice bath. To the cold solution a 1M solution of phosgene in toluene (8.5 mL) was added. The solution was stirred for *ca.* 1 h at 0 °C. The reaction mixture was then filtered to remove pyridinium chloride. To the filtrate 4-aminobenzoic acid (1.74 g, 12.7 mmol) was added. The reaction mixture was stirred for 12 h at room temperature. A 6M solution of HCl (25 mL) was then added to extract the free amines. The organic layer was dried and evaporated to give a pink solid. The crude material was washed with cold methanol to yield the crude acid (1.73 g).

The crude acid was converted to the methyl ester for the purpose of purification. The crude acid (1.35 gm, 4.2 mmol) was dissolved in anhydrous methanol (50 mL). The mixture was stirred in an ice bath for 10 min. Thionyl chloride (1.2 mL, 8.4 mmol) was then added dropwise, after which time the reaction mixture was refluxed for 12 h. It was then cooled to room temperature and the crystalline product was filtered. The crude product was further recrystallized with dichloromethane to yield a light pink solid (997 mg, 71%).

The pure ester was then hydrolyzed to obtain the pure acid. The methyl ester (658 mg, 1.97 mmol) was dissolved in methanol–water (40 : 10). Lithium hydroxide monohydrate (124 mg, 2.95 mmol) was added to the reaction mixture which was then refluxed for 8 h, after which time all the solvent was evaporated under reduced pressure and the contents were dissolved in water. The solution was filtered and acidified to precipitate out the product, which was filtered off and dried under vacuum for 5 h (562.2 mg, 89%). $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 12.50 (br s, acid OH), 8.79 (1H, s, aryl NH), 7.78 (2H, d, $J$ = 8.7, PhH), 7.46 (2H, d, $J$ = 8.7, PhH), 6.26 (1H, t, alkyl NH), 3.06 (2H, q, $J$ = 6.0, $NCH_2$), 1.40 (2H, br, $NCH_2CH_2$), 1.23 (14H, br, alkyl chain), 0.83 (3H, t, $J$ = 6.0 Hz, $CH_3$); MS (FAB) *m/z* calcd for $C_{18}H_{28}N_2O_3$: 320.2099, found 320.2084. Analysis: calcd for $C_{18}H_{28}N_2O_3$: C, 67.47; H, 8.81; N, 8.74. Found: C, 67.44; H, 8.80; N, 8.66%.

**Tetrabutylammonium 4-(3-decylureido)benzoate 3b**

To a solution of 4-(3-butylureido)benzoic acid (0.35 g, 1.1 mmol) in methanol was added a 1M solution of tetrabutylammonium hydroxide in methanol (1.1 mL, 1.1 mmol). The solvent was evaporated and the product was dried under vacuum. It was then washed with diethyl ether and dried under vacuum to yield a white powder (0.45 g, 73%). $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 9.95 (1H, br, aryl NH), 7.73 (2H, d, $J = 8.6$, PhH), 7.6 (1H, br, alkyl NH), 7.43 (2H, d, $J = 8.5$, PhH), 3.16–3.03 (10H, ammonium $NCH_2$ and urea $NCH_2$), 1.53 (8H, ammonium $NCH_2CH_2$), 1.38 (2H, m, urea $NCH_2CH_2$), 1.34–1.23 (22H, m, ammonium and urea $CH_2$), 0.91 (12H, t, $J = 7.2$, ammonium $CH_3$), 0.83 (3H, t, $J = 6.8$ Hz, urea $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 172.3, 157.4, 143.9, 131.1, 130.4, 116.6, 77.4, 58.3, 40.1, 32.0, 31.0, 29.9, 29.7, 29.5, 27.4, 23.7, 22.8, 19.6, 14.2, 13.7; MS (FAB) *m/z* calcd for $C_{33}H_{63}N_3O_3$: 561, found 561. Analysis: calcd for $C_{33}H_{63}N_3O_3 \cdot 0.4H_2O$: C, 71.75; H, 11.29; N, 7.38. Found: C, 71.82; H, 11.31; N, 7.31%.

**3-(3-Butylureido)benzoic acid**

In a round bottom flask 3-aminobenzoic acid (1 g, 7.30 mmol) was dissolved in THF (20 mL). Butylisocyanate (1.3 mL, 11.53 mmol) was added by a syringe and the mixture was refluxed overnight. The solvent was then evaporated and the solid residue was washed with hydrochloric acid (1 M). The light pink solid was dissolved in a saturated solution of potassium bicarbonate. The solution was acidified to pH < 1 by hydrochloric acid (2 M). The product was suction filtered, air dried and washed with diethyl ether to yield a light pink powder (1.0 g, 58.1%), m.p. 231–233°. $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 0.87 (t, $J = 7.2$, 3H, $CH_3$), 1.24–1.42 (m, 4H, $CH_2$), 3.07 (q, $J = 6.3$, 2H, urea $CH_2$), 6.12 (br, 1H, urea), 7.30 (t, $J = 7.8$, 1H, PhH), 7.45 (d, $J = 7.5$, 1H, PhH), 7.57 (d, $J = 7.5$ Hz, 1H, PhH), 8.04 (s, 1H, PhH), 8.60 (s, 1H, urea H); $^{13}$C NMR [75 MHz, $(CD_3)_2SO$] δ 13.7, 19.6, 31.9, 118.3, 121.8, 128.8, 131.2, 140.9, 155.2, 167.5; MS (EI) *m/z* calcd for $C_{12}H_{16}N_2O_3$: 236.2706, found 236.1160. Analysis: calcd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.82; N, 11.85. Found: C, 61.10; H, 6.85; N, 11.79%.

**Tetramethylammonium 3-(3-butylureido)benzoate 4a**

3-(3-Butylureido)benzoic acid (500 mg, 2.12 mmol) was dissolved in methanol, and a 25% solution of tetramethylammonium hydroxide in methanol (0.77 mL, 2.12 mmol) was added to the acid solution. The solvent was evaporated and the product was dried under vacuum, and washed several times with acetone to obtain a powder (569 mg, 87%), m.p. 190–193°. $^1$H NMR [300 MHz, $(CD_3)_2SO$] δ 0.88 (t, $J = 7.2$, 3H, alkyl $CH_3$), 1.26–1.461 (m, alkyl $CH_2$), 3.07 (s, 14H, urea $CH_2$ and ammonium $CH_3$), 7.08 (t, $J = 7.8$, 1H, PhH), 7.40 (d, $J = 7.5$, 1H, PhH), 7.71 (s, 1H, PhH), 7.91 (d, $J = 7.8$ Hz, 1H, PhH), 9.12 (br, 1H, urea H), 10.68 (s, 1H, urea H); $^{13}$C NMR [75 MHz, $(CD_3)_2SO$] δ 13.9, 19.8, 32.1, 54.3, 118.5, 121.4, 126.9, 140.5, 141.2, 156.6, 170.5; MS (FAB) *m/z* calcd for $C_{16}H_{27}N_3O_3$: 309.2052, found 309. Analysis: calcd for $C_{16}H_{27}N_3O_3 \cdot H_2O$: C, 58.68; H, 8.93; N, 12.84. Found: C, 58.38; H, 8.83; N, 12.94%.

**Tetrabutylammonium 3-(3-butylureido)benzoate 4b**

3-(3-Butylureido)benzoic acid (450 mg, 1.91 mmol) was dissolved in methanol, and a 1M solution of tetrabutylammonium hydroxide in methanol (2.0 mL, 2.0 mmol) was added to the acid solution. The solvent was evaporated and the product was dried under vacuum and washed several times with acetone to afford light brown crystals (727 mg, 77.0%), m.p. 180–181°. $^1$H NMR (300 MHz, $CDCl_3$) δ 0.79 (m, 15H, alkyl and ammonium $CH_3$), 1.16–1.37 (m, 15H, alkyl and ammonium $CH_2$), 1.46–1.56 (m, 2H, alkyl $CH_2$), 2.77–2.80 (m, 8H, ammonium $CH_2$), 3.12 (t, $J = 7.2$, 2H, alkyl $CH_2$), 7.09 (t, $J = 7.8$, 1H, PhH), 7.56 (d, $J = 7.2$, 1H, PhH), 7.89 (s, 1H, PhH), 7.93 (s, 1H, urea), 8.08 (d, $J = 8.1$ Hz, 1H, PhH), 10.03 (s, 1H, urea); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.9, 19.4, 20.3, 23.6, 32.6, 39.5, 58.1, 118.6, 119.2, 122.0, 128.0, 140.5, 140.7, 157.2, 171.1; MS (FAB) *m/z* calcd for $C_{28}H_{51}N_3O_3$: 477.3930, found 477. Analysis: calcd for $C_{28}H_{51}N_3O_3 \cdot 0.3H_2O$: C, 69.61; H, 10.77; N, 8.70. Found: C, 69.74; H, 10.75; N, 8.74%.

**Crystallography**

**Crystal data, collection and refinement details for 3a.** $C_{28}H_{51}N_3O_3$, f.w. 477.73, orthorhombic, space group *Pcnb*, $a = 15.941(3)$, $b = 16.213(3)$, $c = 23.528(5)$ Å, $U = 6082(2)$ Å$^3$, $Z = 8$, $D_{calc} = 1.043$ Mg m$^{-3}$, $F(000)$ 2112, crystal size $0.09 \times 020 \times 0.27$ mm.

$T = 293(2)$K, θ range 3.35–59.02°, $-14 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 14$, $-26 \leqslant l \leqslant 26$, 9570 reflections collected, 2529 independent reflections ($R_{int} = 0.0665$).

Full matrix least-squares refinement on $F^2$, 317 parameters, g.o.f. 1.049, $R$ indices [$I < 2\sigma(I)$]: $R1$ 0.0826, $WR2$ 0.1719, largest diff. peak and hole 0.126, −0.144 e Å$^{-3}$.

**Crystal data, collection and refinement details for 4a.** $C_{16}H_{27}N_3O_3 \cdot H_2O$, f.w. 327.42, monoclinic, space group $P2_1$, $a = 8.660(2)$, $b = 19.715(4)$, $c = 11.807(2)$ Å, β = 105.66(6), $U = 1941.0(7)$ Å$^3$, $Z = 4$, $D_{calc} = 1.007$ Mg m$^{-3}$, $F(000) = 640$, crystal size $0.10 \times 0.18 \times 0.18$ mm.

$T = 293(2)$ K, θ range 3.89–62.03°, $0 \leqslant h \leqslant 7$, $0 \leqslant k \leqslant 22$, $-13 \leqslant l \leqslant 13$, 2506 reflections, 2280 independent reflections ($R_{int} = 0.0268$).

Full-matrix least-squares refinement on $F^2$, 379 parameters, g.o.f. 1.088, $R$ indices [$I < 2\sigma(I)$]: $R1$ 0.0944, $WR2$ 0.2644, largest diff. peak and hole 0.722 and −0.388 e A$^{-3}$.

CCDC reference number 440/011.

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$$n\mathrm{M} \overset{K}{\rightleftharpoons} \mathrm{N}, \quad K = \frac{[\mathrm{N}]}{[\mathrm{M}]^n}$$

The molar ratio of the monomer, $X = [\mathrm{M}]/[\mathrm{M}_0]$, is obtained using the equation:

$$[\mathrm{M}_0] = X[\mathrm{M}_0] + nKX^n[\mathrm{M}_0]^n$$

where $[\mathrm{M}_0]$ is the original concentration of the monomer. The chemical shift is then calculated by using: $\delta_{\mathrm{calc}} = \delta_{\mathrm{M}} X + \delta_{\mathrm{N}} (1 - X)$, where $\delta_{\mathrm{M}}$ is the chemical shift of the monomer and $\delta_{\mathrm{N}}$ is the chemical shift of the oligomer. Finally, the chi square value is calculated by using the expression: $S = \sum^i (\delta_{\mathrm{calc}} - \delta_{\mathrm{obs}})^2$.

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