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Low-density hydrogen-bonded networks in crystals and at the air/water interface

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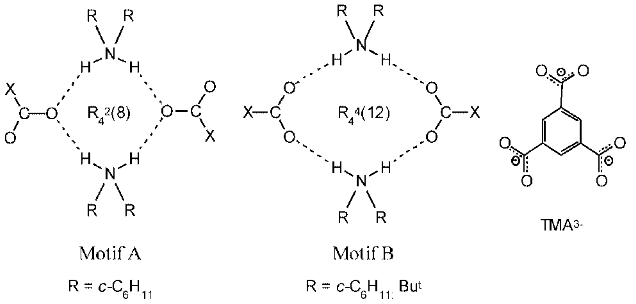
Trimesic acid and various alkylamines assemble into ordered two-dimensional hexagonal hydrogen-bonded networks in both bulk crystals and at the air/water interface.

Interest in low-density open organic frameworks, assembled by non-covalent interactions, has increased significantly owing to their potential application as designer solids for separations, catalysis, and electronic materials.[1] Controlling the structure of porous networks can be complicated by interpenetration of equivalent frameworks[2] and the influence of guest or solvent molecules on structural isomerism of the framework.[1d,3] A recent study of a single crystal of a 3 : 1 complex consisting of dicyclohexylamine and trimesic acid (H_3TMA), crystallized from a 1 : 1 mixture of butan-1-ol and methanol,[4] revealed a low-density hydrogen-bonded network with the 'chicken-wire' motif A, rather than the more symmetrical structural isomer based on motif B. We report herein, three new compounds that contain the cyclic $R_4^4(12)$ motif B,[5] in which both carboxylate oxygen atoms form hydrogen bonds with the dialkylammonium protons. The formation of these compounds illustrates the sensitivity of structural isomerism to different guest molecules. We also demonstrate that these hydrogen-bonded motifs can be generated at the air/water interface from long chain aliphatic amines and H_3TMA.



Motif A
R = c-C_6H_{11}

Motif B
R = c-C_6H_{11}, Bu^t

Vapor diffusion of acetone into methanol or isopropyl alcohol solutions containing H_3TMA and dicyclohexylamine afforded single crystals of $[NH_2(c\text{-}C_6H_{11})_2{}^+]_3[TMA^{3-}]\cdot Me_2CO\cdot 0.5MeOH$ **1** and $[NH_2(c\text{-}C_6H_{11})_2{}^+]_3[TMA^{3-}]\cdot 2.5\ Me_2CHOH$ **2**, respectively. Similarly, vapor diffusion of acetone and di-*tert*-butylamine into an isopropyl alcohol solution of H_3TMA afforded single crystals of $[NH_2(Bu^t)_2{}^+]_3[TMA^{3-}]\cdot Me_2CO$ **3**. Single crystal X-ray diffraction reveals 2D hydrogen-bonded 'honeycomb' networks in each of these materials.† These networks can be viewed as expanded versions of the 'chicken-wire' motif reported for H_3TMA alone.[2] Pairs of ammonium cations acts as 'spacer' molecules between pairs of carboxylate substituents on the TMA^{3-} anions as depicted in motif B. The 2D sheets pucker to different extents in these structures, reflecting an intrinsic flexibility that enables this network architecture to persist despite the differently sized alkyl groups and solvent molecules included within the networks. Nevertheless, the formation of motif B apparently is quite sensitive to the crystallization solvent, given that motif A was observed in methanol solvated crystals grown from butan-1-ol–methanol solutions.

Compound **1** crystallizes in the space group $P\bar{1}$ and exhibits two crystallographically independent flat 2D hydrogen-bonded layers (Fig. 1). The cyclohexyl substituents of one of these layers project into the hexagonal pores, with six cyclohexyl groups lying in the midplane of the pore, three projecting above the plane, and the remaining three projecting below the plane. The second layer (not shown) also has the identical honeycomb motif but the cyclohexyl substituents are twisted out of the layer plane to a greater extent. These layer structures reflect the flexibility of the hydrogen bonds and the ability of the carboxylate groups to rotate around the C–C bond. The two independent layers alternate along the *a* axis with the pores overlapping, creating a continuous channel along this direction. This contrasts with the previously reported methanol solvate, which crystallized in the hexagonal space group $P6_3$ and exhibited 2D hydrogen-bonded sheets that were organized along the six-fold screw axis such that pores were not continuous. Disordered acetone and methanol molecules occupy the pores in **1**, filling the void space not occupied by the cyclohexyl groups. The guest stoichiometry was determined by thermal gravimetric analysis and ^1H NMR spectroscopy.

Compound **2** crystallizes in space group $P\bar{1}$ and exhibits hydrogen-bonding motif B. However, two carboxylate groups of each TMA^{3-} anion each have one oxygen that is hydrogen bonded to the dialkylammonium protons as well as an isopropyl alcohol molecule that resides below the plane of the 2D hydrogen-bonded sheet. Each puckered 2D sheet can be described as interconnected hexagons with chair-like conformations. If the hexagon is defined by the centroids of the TMA^{3-}

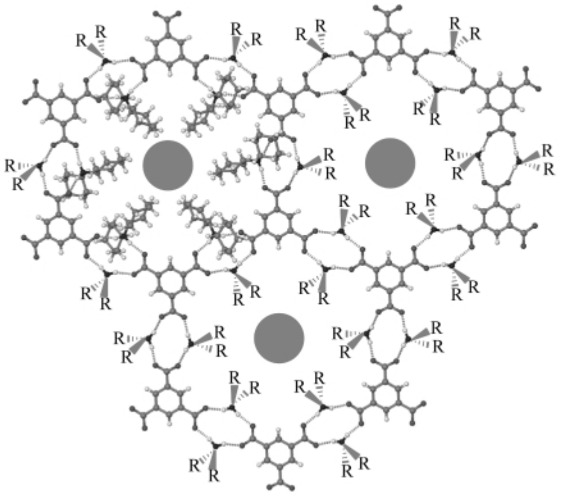


Fig. 1 A portion of one of the two unique 2D hydrogen-bonded networks in **1**. Of the twelve cyclohexyl substituents on the interior of each pore, six project along the midplane of the pore while the remaining six project above or below the plane. The pore at the upper left is depicted with all its cyclohexyl substituents; in the remaining two pores these have been denoted as R for simplicity. The disordered guest molecules are depicted by the circles in the center of the pores.

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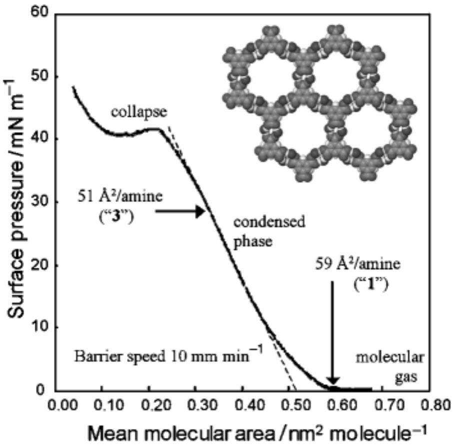

Fig. 2 Pressure–area isotherm of ODA over an aqueous H_3TMA subphase, indicating a molecular area of *ca.* 59 Å^2/amine at lift-off, and 51 Å^2/amine before collapse. The insert depicts the *bc* plane of compound **1** (cyclohexyl groups and guest molecules omitted for clarity), which has a calculated area matching that obtained from the Langmuir isotherm.

anions, the torsion angles associated with the chair-like conformations are 19.1, 16.2 and 18.4°. The hexagonal pores in adjacent sheets are slightly offset but still create a continuous channel, along the *a* axis, that is filled with disordered isopropyl alcohol guests.

Compound **3** crystallizes in the space group $P2_1/n$, and exhibits motif B with hydrogen-bonded sheets consisting of chair-like hexagons that are more severely puckered than in **2**, with torsion angles measuring 22.9, 23.9 and 25.5°. Two acetone molecules occupy the void space not occupied by the *tert*-butyl groups of the amines within each pore.

The bulk structure of organic crystals can often be described as 2D molecular layers that stack in the remaining third dimension. Consequently, these layer motifs can be used as models for the design of monolayers on solid substrates and at the air/water interface. The latter requires amphiphiles with polar head groups capable of organizing at the air/water interface into motifs that mimic the structure of the 2D layers in the bulk crystals.[3a,6]

The pressure–area isotherm measured for the long chain amphiphile octadecylamine (ODA), spread over an aqueous subphase of H_3TMA, exhibits lift-off at a molecular area of 59 Å^2/amine. Extrapolation of the linear compression regime afforded a molecular area of 51 Å^2/amine (Fig. 2). In contrast, a molecular area of *ca.* 20 Å^2/amine was measured when ODA was spread over a basic subphase without H_3TMA.[7] Similar isotherms were collected for methyloctadecylamine (MODA) and dioctadecylamine (DODA), both exhibiting linear compression regimes that were consistent with an area of 54 Å^2/amine.‡ The molecular areas measured from the isotherms collected over H_3TMA lie within the range of the molecular areas occupied by the 2D hydrogen-bonded networks in **1**–**3** (58.6, 56.6 and 51.5 Å^2/amine, respectively). This strongly supports the formation of a 2D porous hydrogen-bonded monolayer at the air/water interface having motif B. Notably, the molecular area for the methanol solvate of **1** and **2** (motif A), based on the reported crystal structure, is only 45 Å^2/amine. Furthermore, the range of lift-off and extrapolated values reflected by the different isotherms, suggests that the monolayers possess the flexibility evident from the bulk crystalline networks.

We anticipate that porous Langmuir monolayers can serve as structural mimics of isostructural porous 2D networks in crystalline solids. These monolayers, for which interpenetration is not possible, may promote the nucleation and growth[6,8] of crystalline phases containing such networks. Porous monolayers, transferred to permeable solid substrates by the Langmuir–Blodgett method, may also be useful as size exclusion membranes in which the pore sizes can be adjusted by molecular design.

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Notes and references

† *Crystal data*: for **1**: $C_{45}H_{75}N_3O_6\cdot(CH_3)_2CO\cdot0.5CH_3OH$, triclinic, $P\bar{1}$, a = 16.9805(3), b = 19.5242(4), c = 20.0428(4) Å, α = 116.268(1), β = 111.491(1), γ = 95.189(1)°, U = 5284.2(2) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 0.062 mm^{-1}, 35303 reflections measured, 17825 unique (R_{int} = 0.0289) which were used in all calculations. There is disordered solvent present in this structure. Attempts were made to model this, but were unsuccessful since there were no obvious major sire occupations for the solvent molecules. PLATON/SQUEEZE[9] was used to correct the data for the presence of the disordered solvent. A potential solvent volume of 1091.1 Å^3 was found. 300 electrons per unit cell worth of scattering were located in the void. The stoichiometry of solvent was calculated independently by NMR and TGA to be one molecule of MeOH and two molecules of acetone per unit cell, which results in 228 electrons per unit cell. The modified dataset improved the R1 value by *ca.* 10%; final R1 = 0.0563, wR2 = 0.1379.

For **2**: $C_{45}H_{75}N_3O_6\cdot2.5(CH_3)_2CHOH$, triclinic, $P\bar{1}$, a = 10.5401(6), b = 15.815(1), c = 18.711(1) Å, α = 107.648(1), β = 105.627(1), γ = 97.211(1)°, U = 2788.3(3) Å^3, T = 173 K, Z = 2, μ(Mo-Kα) = 0.074 mm^{-1}, 22227 reflections measured, 9779 unique (R_{int} = 0.0385) which were used in all calculations. Two isopropyl alcohol molecules were found and refined in the structure. The structure contains disordered solvent in a channel along (x,1/2,1/2). Attempts to model this were unsuccessful. PLATON/SQUEEZE was used to correct the data for the presence of the disordered solvent. A potential solvent volume of 246.9 Å^3 located in the above mentioned channel was found. 38 electrons per unit cell worth of scattering were located in the void. The electron count suggests the presence of *ca.* one isopropyl alcohol molecule per unit cell. The modified dataset improved the R1 value by *ca.* 6%; final R1 = 0.0642, wR2 = 0.1895.

For **3**: $C_{45}H_{75}N_3O_6\cdot(CH_3)_2CO$, monoclinic, $P2_1/n$, a = 9.745(1), b = 18.486(2), c = 23.157(2) Å, β = 101.644(3)°, U = 4090.0(5) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 0.073 mm^{-1}, 30377 reflections measured, 7227 unique (R_{int} = 0.0828) which were used in all calculations; final R1 = 0.0600, wR2 = 0.1752. The dataset was checked for twinning and disordered solvent, however, no evidence for either was found.

CCDC 182/1580. See http://www.rsc.org/suppdata/cc/a9/a910252n/ for crystallographic files in .cif format.

‡ Interestingly, the isotherm of DODA initially reveals a linear compression feature corresponding to 94 Å^2/amine, but collapses at 23 mN m^{-1} to the linear region associated with the 54 Å^2/amine value. We surmise that this value corresponds to a condensed phase in which one of the alkyl chains lies at the air/water interface until increased compression drives both alkyl chains away from the air/water interface to form a 2D structure similar to the monoalkylamine layers.

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