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ARTICLE TYPE

An Unsaturated Hydrogen Bonded Network Generated from Three-fold Symmetric Carbamates

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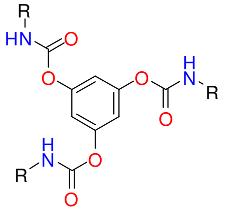
An new hydrogen bonded network self-assembled under mild conditions from benzene-1,3,5-triyl tris(butyl-carbamate) or benzene-1,3,5-triyl tris(hexyl-carbamate). One of the carbonyl group in the tri-carbamate does not form a C=O···H-N hydrogen bond in the sheet-like structure. Although the building blocks are only different in carbon numbers of the sides chains, this 2D unsaturated hydrogen bonded network is different from the saturated one self-assembled from benzene-1,3,5-triyl tris(propyl-carbamate). The lamellar structures were studied and compared by using their melting points, NMR, FT-IR and single crystal X-ray diffraction.

Organic sheets are highly desired and can be found in many natural applications such as the *β*-pleated sheet of polypeptides and lipid bilayer in cell membrane.[1,2,3] Recently, our research group has discovered and studied a series of hydrogen bonded sheets self-assembled from three-fold symmetric triamides or tri-carbamates.[4,5,6] These organic sheet have displayed chirality that is generated from the achiral molecules with stereogenic axes (*supramolecular atropisomer*)[4,5] By introducing cyclohexyl side chains onto the surface of the carbamate sheet, the derived two-dimensional (2D) hydrogen bonded framework has demonstrated application in host-guest chemistry.[6] Another significant characteristic of the hydrogen bonded sheets is the structural adaptability and generality. To adapt the structural variations of the supramolecular building blocks, the hydrogen bonded networks were changed correspondingly while the lamellar structures remained unaltered. Herein, we report an unsaturated hydrogen bonded sheet obtained from three-fold symmetric carbamates.

Just as their reported analogue **C-3** (Scheme. 1),[5] the carbamates **C-4** and **C-6** were readily synthesized from the reaction of phloroglucinol with 1-isocyanatobutane and isocyanatohexane, respectively.[5, 7] The three carbamates are soluble in a variety of organic solvents such as chloroform, ethyl acetate, dichloromethane, acetone, acetonitrile, THF, and DMSO. Self-assembly behaviour of the tri-carbamate **C-6** was then examined in solvents. Evidence of intermolecular H-bonding can be seen in the ^{1}H NMR spectra in $CDCl_3$ (see Fig. S5 in the ESI†). As concentration of the solution increase from 3.0 to 200.0 mM, the chemical shift of amide proton gradually shifted to downfield. Hydrogen binding decreases the electron density around the amide proton, thus moving its peak to downfield. The chance to form intermolecular amide hydrogen bonding, –N–H···O=C, in a concentrated solution is higher, and therefore the peak appears at downfield.[8,9]

A side-to-side comparison of the three tri-carbamates revealed several interesting differences. The melting points (m.p.) of **C-4** and **C-6** are both around 130 °C, which is clearly lower than that of **C-3** (144 °C) although their molecular weights are higher. While the FT-IR spectra of **C-4** and **C-6** are nearly identical, they are different from that of **C-3**, especially in the stretching wavenumbers of the amide C=O (around 1700 cm^{-1}) and N-H bonds (around 3300 cm^{-1}). There are three peaks near 1700 cm^{-1} in the spectra of the **C-4** and **C-6,** but only two in the spectrum of **C-3** (Fig. 1 and the ESI†). Considering the three carbamates contain the same functional groups, the IR and m.p. differences indicated different types of hydrogen bonding patterns.

Similar to **C-3**, high quality single crystals of the **C-4** and **C-6** were obtained by slowly evaporating acetonitrile and acetonitrile /dichloromethane solutions of the carbamates, respectively. On one hand, the X-ray structures showed that 2D hydrogen bonded networks are presented in the crystals of all three carbamates. The polar amide hydrogen bonded networks are sandwiched by two layers of non-polar alkyl chains forming sheet structures in all three cases. On the other hand, the **C-4** and **C-6** adopt the same hydrogen bonding network, but quite different from that of **C-3** (see Table 1 and Fig. 2; The **C-6** sheet images are included in the ESI† since it is similar to the **C-4** sheet).



Previous study:
R = $-C_3H_7$ (**C-3**, m.p. 143 -145°C)

This study:
R = $-C_4H_9$ (**C-4**, m.p. 130 -132 °C)
R = $-C_6H_{13}$ (**C-6**, m.p. 130 -131 °C)

Scheme 1 Structural formula and m.p. of the three tri-carbamates.

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†Electronic Supplementary Information (ESI) available: Experimental procedure, full characterzation and spectra, and crystallographic data in CIF format see DOI: 10.1039/b000000x/

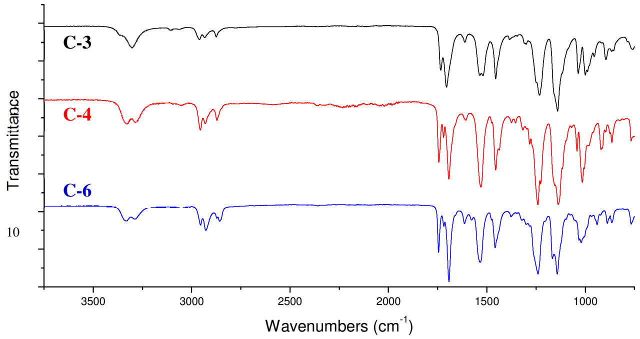

Fig. 1 Comparison of the FT-IR spectra of the three tri-carbamates.

The tri-carbamate **C-3** crystallized in the orthorhombic Fdd2 space group and each tri-carbamate molecule is connected to five neighbours through six intermolecular hydrogen bonds between N-H and C=O groups of the three carbamate groups (Fig. 2a and 2c).[5] Specifically, each tri-carbamate molecule is connected to one closest neighbour by two hydrogen bonds forming a cyclic supramolecular dimer. Each dimer is held together with four neighbouring dimers by eight hydrogen bonds. The crystal structures consist of a supramolecular sheet extended in the crystallographic *ac* plane through a fully saturated hydrogen bonded network. In contrast, the tri-carbamates **C-4** and **C-6** crystallized in the monoclinic $P2_1/c$ space group and each tri-carbamate molecule is connected to four neighbours through six intermolecular hydrogen bonds between N-H and C=O groups of the three tri-carbamates. The crystal structures consist of a supramolecular sheet extended in the crystallographic *bc* plane through an unsaturated hydrogen bonded network (Fig. 2b and 2d). In other words, one of the C=O group (marked by the red arrow in Fig. 2b) formed two hydrogen bonds with two N-H

Table 1. Crystal Data of the Three Tri-carbamates

Crystals	C-3[5]	C-4	C-6
CCDC #	873164	987316	987317
Formula	$C_{18}H_{27}N_3O_6$	$C_{21}H_{33}N_3O_6$	$C_{27}H_{45}N_3O_6$
FW	381.43	423.50	507.66
Cryst. Size [mm]	0.62,0.61,0.16	0.46,0.17,0.05	0.34,0.17,0.02
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group, Z	Fdd2, 16	$P2_1/c$, 4	$P2_1/c$, 4
a (Å)	13.4049(4)	17.4350(4)	21.2940(14)
b (Å)	48.9616(14)	13.8312(3)	13.8436(10)
c (Å)	12.2121(4)	9.7128(2)	9.8230(7)
α (°)	90.00	90.00	90.00
β (°)	90.00	96.5590(10)	91.467(4)
γ (°)	90.00	90.00	90.00
V (Å^3)	8015.1(4)	2326.88(9)	2894.7(3)
Temp. (K)	100(2)	100(2)	100(2)
ρcalc [g/cm^3]	1.264	1.209	1.165
μ [mm^{-1}]	0.095	0.731	0.663
Radiation Type	Mo	Cu	Cu
F(000)	3264	912	1104
No of measured refl.	42256	30206	12037
No of independent refl.	6096	4025	4804
No of refl. (I ≥ 2σ)	5905	3617	3992
R1/wR2 (I ≥ 2σ) [%]	2.73/7.63	2.98/7.68	4.87/12.85
R1/wR2 (all data) [%]	2.98/8.14	3.38/7.99	5.79/13.36
Average C=O···H-N H-bond length (Å)	2.90(5)	2.90(1)	2.93(2)

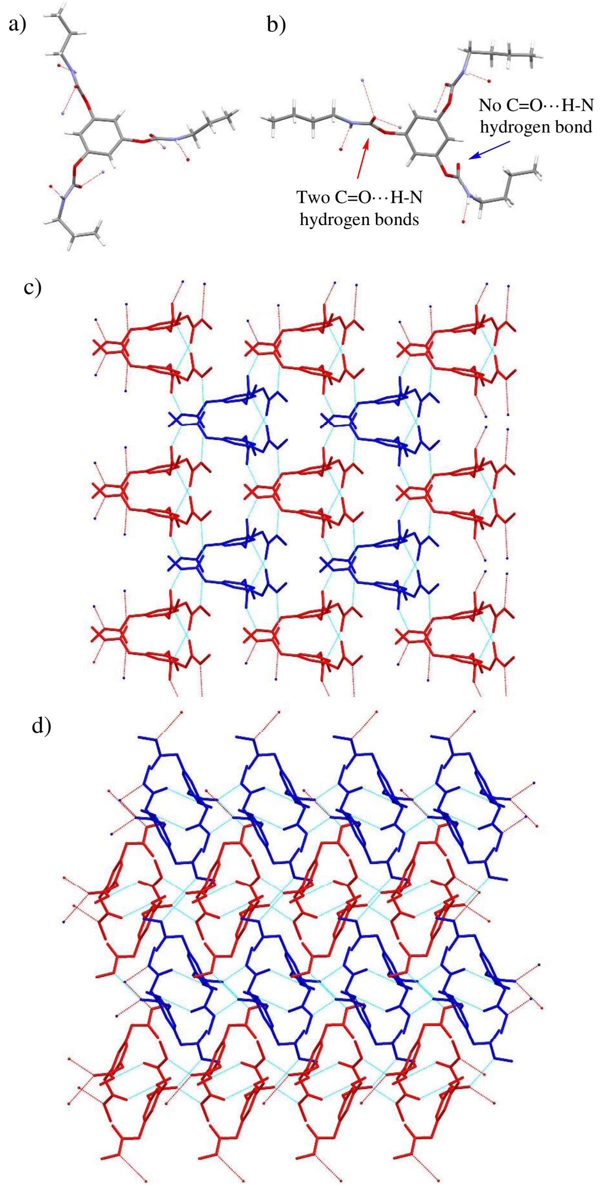

Fig. 2 Comparison of **C-3** and **C-4** crystal structures: (a) The red dash lines represent the six hydrogen of each **C-3** molecule in the sheet; (b) The red dash lines represent the six hydrogen of each **C-4** molecule. The red arrow shows the C=O with two hydrogen bonds and the blue arrow show the C=O without hydrogen bonding; (c) the chiral sheet backbone of tri-carbamate **C-3**. (Each side chain is replaced with a carbon atom for simplicity and hydrogen bonded dimers are shown in different colors for clarity); (d) the racemic hydrogen bonded sheet backbone of tri-carbamate **C-4**. (Neighboring hydrogen bonded ribbons are shown in two colors for clarity.)

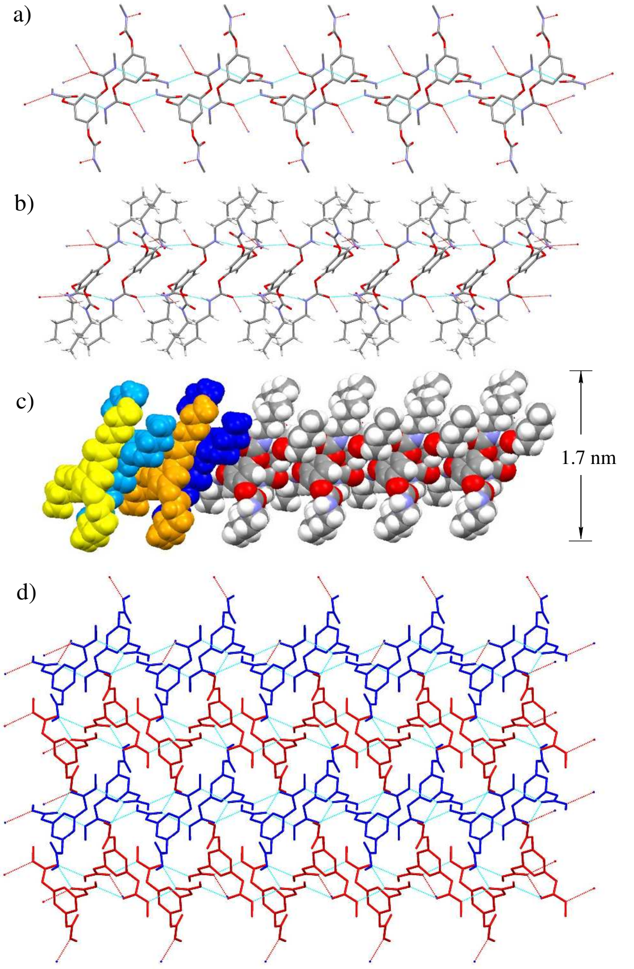

Fig. 3 Hydrogen bonded ribbon and sheet of tri-carbamate **C-4** (a) The hydrogen bonded ribbon (hydrogen atoms are omitted and the side chains are replaced with carbon atoms for simplicity); (b) a side view of the hydrogen bonded ribbon; (c) hydrogen bonded ribbon in space-filling style showing the height; (d) the hydrogen bonded sheet backbone. (Neighboring hydrogen bonded ribbons are shown in two different colors for clarity.)

groups of two neighbouring tri-carbamate molecules while another C=O group (marked by the blue arrow in Fig. 2b) does not form a C=O···H-N hydrogen bond.[10,11]

The second difference between the **C-3** and **C-4** (**C-6**) crystals is packing of the sheets. One of three *n*-propyl arms in crystal **C-3** lied within the plane of the hydrogen bonded network to fill up the space between the supramolecular dimers. There are grooves on the surface of the **C-3** sheet, so the neighbouring sheets are packed like meshing gears to achieve close packing.[5] In contrast, there is no space between the hydrogen bonded network of the **C-4** sheet and all the non-polar alkyl chains point away from the polar hydrogen bonded networks. Although there are slightly periodic fluctuations, no gap or groove occurs on the surfaces of the **C-4** sheet.

Another substantial difference is the chirality of the sheets. Each tri-carbamate molecule contains three stereogenic axes (C_{Ar}-O). The seven atoms, C_A-O-(C=O)NHC_R, within each carbamate in all the three carbamate sheets are nearly planar. Each carbamate group is partially tilted with respect to the core aryl ring to fulfill requirements of the hydrogen bonds' orientations and close packing of the molecules. Instead of a C_3-symmetric conformation,[12,13] one of the three carbamate groups is oriented in the opposite direction. In the supramolecular atropisomer,[4,5,14] the hydrogen bonds do not allow the carbamate groups to rotate freely around the C_{Ar}-O axes. Thus, a three dimensional chiral conformation is fixed in the hydrogen bonded network. In the chiral sheet of **C-3**, all the tri-carbamate molecules within the hydrogen bonded sheet adopt the same conformation. In the racemic sheets of **C-4** and **C-6**, supramolecular enantiomers present next to each other within each sheet.

A close examination of the **C-4** (**C-6**) sheet unveiled that each tri-carbamate molecule connects with two neighbours by four amide hydrogen bonds leading to a supramolecular ribbon (Fig 3a-c). The ribbons then are glued together side by side via the other two hydrogen bonds on each molecule (Fig 3d and 2d). Evidently, the force holding the supramolecular ribbon together is stronger than that between the ribbons due to the different numbers of hydrogen bonds. To understand the packing of the tri-carbamate molecules, one can regard this new organic lamellar crystal as a hierarchical structure[1,15]: primary structure - hydrogen bonded ribbon; secondary structure - supramolecular sheet held together by hydrogen bonding and the hydrophobic effect between peripheral non-polar alkyl chains; and tertiary structure - a lamellar crystal based on London force between the sheets.

Melting temperature is a typical thermodynamic parameter related to the breaking of intermolecular forces in solid-state molecular assemblies.[16,17] The melting points of three tri-carbamates are comprehensible by comparing the crystal structures. Tri-carbamate **C-3** has the highest melting point because it forms a fully saturated hydrogen bonded network and the neighbouring sheets are packed like meshing gears. The relative high density of **C-3** also indicates the efficient packing in the solid-state. Although **C-4** and **C-6** have nearly identical packing, the average hydrogen bonds of **C-6** is 0.03 Å longer, which indicates weaker hydrogen bonding network (Table 1 and ESI[†]). The density of **C-6** is also about 4% lower than that of **C-4**. These differences may offset their difference in molecular weight leading to similar melting points.

In summary, a new hydrogen bonded sheet was yielded from three-fold symmetric tri-carbamates with *n*-butyl or *n*-hexyl side chains. This 2D supramolecular structure was hold together by an unsaturated hydrogen bonded network while a similar tri-carbamate with *n*-propyl side chains led to a saturated one. Together with a number of reported 2D saturated hydrogen bonded networks, the discovery of the unsaturated hydrogen bonded sheet further demonstrated the variety and adaptability of the sheet structures.

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