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# Water templated hydrogen-bonded network of pyridine amide appended carbamate in solid state

Kumaresh Ghosh<sup>a,\*</sup>, Suman Adhikari<sup>a</sup>, Roland Fröhlich<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Kalyani, Kalyani, Nadia 741235, India <sup>b</sup> Organisch-Chemisches Institut, Universität Münster, Corrensstraße 40, D-48149, Münster

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#### Abstract

The pyridine amide appended carbamates 1 and 2 have been synthesized and their hydrogen-bonded self-assemblies in solid state have been described. The self-association pattern is dependent on the nature the anchored group of the carbamate moiety and influenced by water inclusion. Inclusion of water molecule gives a ladder type hydrogen bonded assemblies with cavities.

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### 1. Introduction

The rational design of new solid-state structures is central to a wide variety of applications in crystal engineering and supramolecular chemistry [1-4]. A particular goal, therefore, involves the construction of solids with an appropriate ordered and predictable arrangement of two or more molecular components through specific noncovalent interaction, specifically hydrogen bond which has the pivotal role in molecular recognition studies by synthetic receptors as well as in the formation of supramolecular assembly due to its strength and directional nature relative to other intermolecular interactions [5–10]. Appropriate choice of molecules meeting both geometric as well as energetic interactions allow the controlled formation of different two- and three-dimensional shapes such as sheets [11], ribbons [12], spheres [13], helices [14a], tubes [14b] and zeolitelike 3D network structures with chiral channels [14c] fitted with highly ordered water molecules etc. Such organization of molecular components is controlled by proper hydrogen bonded synthons as well as sometimes by inclusion of small molecules, ions etc [15,16].

In this aspect water is an important molecule, the inclusion of which alters the molecular packing in the crystal [17a]. This is due to various types of hydrogen-bonding possibility present within the simple structure of water. It can either function as double hydrogen bond donor and a single hydrogen bond acceptor in simple hydrate or double hydrogen bond donor and double hydrogen bond acceptor in clathrate hydrates. There are various reports on hydrogen-bonded water clusters in the form of hexamers [17b], octamers [17c], decamers [17d] and onedimensional (1D) infinite water chains [17e] in different crystal hosts. The structures of such hydrogen bonded water clusters continue to attract attention since they play a crucial role in contributing to the stability and function of biological assemblies [17f]. In our continued research in molecular recognition and supramolecular chemistry [18-19] we report here the synthesis and solid state hydrogen bonding assembly of the pyridine amide appended carbamates 1 and 2, for the first time, with a view of establishing the hydrogen bonding nature of carbamate with the complementary pyridine amide motif.

The compounds **1** and **2** were synthesized according to the Scheme 1 and were isolated in good yield as white solids.

## 2. Experimental

## 2.1. General procedure

To a stirred solution of amine 4 [20] (1 equiv.) in dry dichloromethane triphosgene (1 equiv.) was added. After stirring for 1 h at room temperature dry alcohol (1 equiv.) was added drop wise and the mixture was left overnight stirring. The reaction was quenched with aqueous NaHCO<sub>3</sub> (20 ml), and the organic layer was separated. The aqueous layer was extracted with

<sup>\*</sup> Corresponding author. Tel.: +91 33 25828750; fax: +91 33 25828282. *E-mail address:* ghosh\_k2003@yahoo.co.in (K. Ghosh).



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Scheme 1.

dichloromethane and the combined organic layers were dried  $(Na_2SO_4)$  and evaporated to white solid.

Carbamate 1: The compound was purified by column chromatography using 2:1 (pet ether: ethyl acetate) as eluant and was collected as white solid, m.p 166 °C, 80% yield, <sup>1</sup>H-NMR (300 MHz,  $d_6$ -DMSO):  $\delta$  10.49 (s, 1H), 9.97 (s, 1H), 7.99 (d, J=9 Hz, 3H), 7.70 (t, J=9 Hz, 1H), 7.56 (d, J=9 Hz, 2H), 7.01(d, J=9 Hz, 1H), 4.16 (q, J=6 Hz, 2H), 3.35 (bs for H<sub>2</sub>O), 2.45 (s, 3H), 1.27 (t, J=6 Hz, 3H). FT-IR (KBr)  $\nu_{max}$  3129, 1712, 1661, 1601, 1454, 1401 cm<sup>-1</sup>, Mass (FAB<sup>+</sup>): 316 [(M<sup>+</sup> + H<sub>2</sub>O) - 1], 300 (M<sup>+</sup> + 1), 282, 192, 227.

Carbamate 2: The compound 2 was also purified by column chromatography using 2:1 (pet ether: ethyl acetate) and was obtained as white solid, m.p 156 °C, yield 75–80%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (s, 1H), 8.16 (d, J=10 Hz,1H), 7.89 (d, J=10 Hz 2H), 7.63 (t, J=10 Hz,1H), 7.52 (d, J=10 Hz, 2H), 7.42–7.35 (m, 5H), 6.92 (d, J=10 Hz, 2H), 6.85 (s, 1H),

2

5.23 (s, 2H), 2.48 (s, 3H	). FT-IR (KBr) $\nu_{max}$ :	3446, 3318,	1745,
$1665, 1595, 1226 \text{ cm}^{-1}$			

Single crystals of 1 and 2 were grown up by slow evaporation of ethyl acetate-pet ether and chloroform-pet ether combinations, respectively. All the crystallization experiments were conducted in an unmodified atmosphere and solvents were dried by standard methods, prior to use.

#### 2.2. X-ray crystallography

X-ray intensity data for a selected specimen were collected on Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591 ( $\lambda$ =0.71073 Å). The following programs were used: data collection COLLECT [21], data reduction Denzo-SMN [22], absorption correction SORTAV [23], structure solution SHELXS-97 [24], structure refinement

Table I						
Crystal o	lata and	structure	refinement	for 1	l a	and

	1	2
Empirical formula	C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> *H <sub>2</sub> O	C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>
Formula weight	317.34	361.39
Temperature (K)	293(2) K	198(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, P1(no. 2)	Triclinic, P1 (no.1)
Unit cell dimension (Å)	$a = 8.096(1)$ Å, $\alpha = 92.43(1)^{\circ}$	$a = 4.563(1)$ Å, $\alpha = 92.76(1)^{\circ}$
	$b = 8.660(1) \text{ Å}, \beta = 107.04(1)^{\circ}$	$b = 6.436(1) \text{ Å}, \beta = 91.94(1)^{\circ}$
	$c = 13.456 (1) \text{ Å}, \gamma = 117.07(1)^{\circ}$	$c = 15.300(3) \text{ Å}, \gamma = 92.70(1)^{\circ}$
Volume ( $Å^3$ )	785.9(2)	448.0(2)
Z, calculated density	2, 1.341 Mg/m <sup>3</sup>	1, 1.339 Mg/m <sup>3</sup>
Absorption coefficient (µ)	$0.098 \text{ mm}^{-1}$	$0.091 \text{ mm}^{-1}$
F(000)	336	190
Crystal size	$0.30 \times 0.20 \times 0.15 \text{ mm}$	$0.30 \times 0.15 \times 0.03 \text{ mm}$
Theta range for data collection	1.62–27.89°	2.67–27.83°
Limiting indices	$-10 \le h \le 10, -11 \le k \le 11, -17 \le l \le 17$	$-5 \le h \le 5, -8 \le k \le 8, -19 \le l \le 9$
Reflections collected/unique	8175/3743 ( <i>R</i> (int)=0.054)	4479/2690 (R(int) = 0.0052)
Completeness to theta	99.4%	88.8%
Max. and min. transmission	0.986 and 0.971	0.997 and 0.973
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Goodness-of-fit on $F^2$	1.035	1.032
Final <i>R</i> indices $[I > 2\sigma > I]$	$R1 = 0.055, wR^2 = 0.124$	$R1 = 0.060, wR^2 = 0.147$
<i>R</i> indices (all data)	$R1 = 0.101, wR^2 = 0.143$	$R1 = 0.085, wR^2 = 0.165$
Largest diff. peak and hole	$0.22 \text{ and } -0.20 \text{ e} \text{\AA}^{-3}$	0.21 and $-0.18 \text{ e}\text{\AA}^{-3}$

SHELXL-97 [25], graphics SCHAKAL [26]. The details and results of the analysis are presented in Table 1.

### 3. Results and discussion

Carbamates are interesting synthons in crystal engineering on account of the fact that they exist as *syn* and *anti* rotamers (Fig. 1), with the *anti* rotamer favored by 1.0–1.5 kcal/mol for



Fig. 1. Carbamate rotamers.

steric and electrostatic reasons [27a]. These interesting features of carbamates have been considered in the design of receptors for theobromine alkaloid [27b]. The coupling of such carbamate with complementary pyridine amide in specific design is of keen interest in the context of building up of new-engineered solid in crystal engineering. In this aspect the single crystals of 1 and 2 were grow up by slow evaporation of ethyl acetate-pet ether and chloroform-pet ether combinations, respectively. The crystal data, data collection parameters and analysis statistics are listed in the Table 1 [28].

In the crystal structure of **1** one molecule of water is bonded as water of crystallization to the more basic pyridine nitrogen and crystallizes in space group  $P\overline{1}$ . The SCHAKAL plot with atom numbering scheme is shown in Fig. 2. The bound water molecule typically functions as a double hydrogen bond donor and a double hydrogen bond acceptor and exhibits a symmetric dimer. Each neighbouring dimers are further assembled through hydrogen bonds involving water as spacer in hydrogen bonded network and executes nice water assisted ladder type polymeric assembly (Fig. 3).

It is well known that the preferred hydrogen bond coordination of the water molecule is tetrahedral or planar trigonal [29]. In the present case, the water as bridging entity



Fig. 2. SCHAKAL plot of 1 with atom numbering scheme.



Fig. 3. Hydrogen bonded three-dimensional arrangement of  $1 \cdot H_2O$ .

forms (i) N-H···O hydrogen bond [N3-H3 0.85(2), H3...O20<sup>\*</sup> 2.09(2), N3...O20<sup>\*</sup> 2.933(2) Å, N3–H3...O20<sup>\*</sup>  $173(2)^{\circ}$ , symmetry operation 1-x, 1-y, 1-z] with the more favored anti form of carbamate rotamer, (ii) O-H···N [O20-H20A H20A...N14 0.80(2),2.17(3),020…N14 2.952(2) Å,O20-H20A...N14 169(3)°] hydrogen bond with pyridine ring nitrogen (iii) O-H···O hydrogen bond [O20-H20B 0.90(3), H20B…O11<sup>\*\*</sup> 2.08(3), O20…O11<sup>\*\*</sup> 2.977(2) Å, O20-H20B…O11\* 171(2)°, symmetry operation x-1, y, z] with pyridine amide carbonyl of the adjacent dimer and (iv) C-H···O hydrogen bonds with H2AB (2.76 Å which is about 0.14 Å shorter than the sum of the van der Waals radii), where H2AB is one of the hydrogens at C2A (ethyl group) thereby giving a tetrahedral arrangement. This tetrahedral hydrogen bond co-ordination of water molecule associates 1 as cyclic dimers via the two nitrogen-water hydrogen bonds and is further connected via the oxygenwater hydrogen bond in the third direction to give a ladder type arrangement. However, in such assembly each macrocycle provides inwardly pointed two diagonal free N12-H12 hydrogen bond donors. These cavities may form inclusions of a range of guest molecules that are both functionally and dimensionally fitted into.

A closer look on the geometrical parameters shows a distance of 3.72 Å between the centers of neighbored pyridine rings (symmetry operation -x, -y, -z) indicating the influence of  $\pi$ - $\pi$  interactions. In contrast, there is no indication for C-H··· $\pi$  interactions (closest distance from H2AA<sup>\*\*\*</sup> to the center of the benzene ring is 3.10 Å; symmetry operation 2-x, 2-y, 1-z).

The presence of anchored water was also supported by the appearance of the peak at 316  $[(M^+ + H_2O) - 1]$  in mass spectrum. The thermal stability of the water molecule in  $1 \cdot H_2O$  was studied by thermogravimetric analysis (TGA) (Fig. 4). The weight loss for water is 5.7% that takes place in the temperature region 25–140 °C and second weight loss occurs after 212 °C.



Fig. 4. TGA plot showing the weight loss of the compound  $1{\cdot}{\rm H_2O}$  on increasing the temperature.

DSC experiment showed two endothermic peaks at  $137^{\circ}$  and  $171 \,^{\circ}$ C. The first endotherm is, therefore, due to dehydration and second one due to melting.

Such water assisted hydrogen bonded architecture of 1 is absent in 2 when benzyl group replaces the ethyl group of the carbamate part. The SCHAKAL plot of 2, which crystallizes in chiral space group P1, is presented in Fig. 5. The packing mode (Fig. 6) indicates a parallel arrangement of the molecules with parallel hydrogen bonds keeping all the pyridines at one end and phenyls on the other end and surprisingly the achiral compound 2 crystallizes in an enantiomorphic space group.



Fig. 5. SCHAKAL plot of 2 with atom numbering scheme.



Fig. 6. Packing plot of 2.

Such arrangement is different from 1 where ethyl chain and pyridine amide lie in opposite directions.

The selective combination of hydrogen bond donors and acceptors of **2** governs the assembly indicating carbamate NH, a better donor and pyridine amide carbonyl oxygen, a better acceptor. In the assembly pyridine rings are 4.563 Å apart (along *a*-axis) and do not show any  $\pi$ -stacking interaction. The presence of phenyl ring in the carbamate moiety possibly plays the key role not to allow any inclusion of water in the network.

In summary, we have thus established that the inclusion of water is dependent on the nature of the group anchored in the carbamate moiety in our examples 1 and 2. Pyridine appended carbamate having normal aliphatic group instead of aliphatic chain containing pendent aromatic group, prefers water inclusion that alters the molecular packing of carbamates. The compound  $1 \cdot H_2O$  is stable hydrate above the boiling point of water and exhibits a unique hydrogen bonding architecture with cavities. Further exploration in this direction is in progress in our laboratory.

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