Comparative Structural Studies on Homologues of Amides and Reverse Amides: Unprecedented 4-fold Interpenetrated Quartz Network, New β-Sheet, and Two-Dimensional Layers

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ABSTRACT: The homologous series of *N,N'*-bis(phenyl)alkanediamides, *N,N'*-bis(3-pyridyl)alkanediamides, and *N,N'*-bis(4-pyridyl)alkanediamides (reverse amides) have been synthesized and crystallized. The crystal structures of these amides were determined and analyzed in terms of hydrogen bonding patterns. Their structural patterns have been compared with those of bis(phenylcarboxamido)alkane, bis(4-pyridinecarboxamido)alkane, and bis(3-pyridinecarboxamido)alkane derivatives (amides). The similarities in supramolecular geometries between the reverse amides and amides were studied and discussed in detail. The interference of pyridyl groups in amide-to-amide hydrogen bonds was found to be more prominent in reverse amides than amides. Conventional β-sheet patterns were not observed in reverse amides containing pyridine groups. The supramolecular patterns in reverse amides are totally deviated from those of amides when they contain 4-pyridyl groups. In this study, we found that the reverse amides form two new β-sheet patterns: one formed via N–H···N and N–H···O hydrogen bonds, whereas the other is formed by the joining of amides via water molecules (N–H···Ow and Ow–H···O). Further, one of these reverse amides found to form a 4-fold interpenetrated network with quartz topology via N–H···N hydrogen bonds.

Introduction

Deliberate design of molecules to build supramolecules in crystals with particular properties has become a very attractive area of research.[1] The productive strategy in crystal engineering is to consider the molecules with functional groups that form robust supramolecular synthons.[2,3] The molecules with carboxylic acid and amide functional groups are usually known to form robust synthons in the absence of other strong hydrogen bonding functional groups.[4,5] Further, understanding the relationship between molecule and supramolecule is most fundamental and an important aspect for successful design in crystal engineering.[6] Such a relationship can be established by the study of a group of crystal structures of compounds containing almost similar functionalities. Recently, we have reported the studies on homologous series of **1**, **3**, and **5** which contain amide and pyridine groups and found that they form identical β-sheet structures in particular when X = $-(CH_2)_6-$, $-(CH_2)_8-$ or $-C_6H_4-$ (Scheme 1).[7] Whereas, when X = $-(CH_2)_4-$, it has been observed that they form 2D layers via amide-to-amide hydrogen bonds.[5] The interference of pyridine in amide-to-amide hydrogen bonds has been found to be minimal in the cases of **3** and **5**. Further, we have proposed a geometric criteria that the interplanar angle (θ) between the aryl (R) and amide moieties should be above 20° in order to form amide-to-amide hydrogen bonds. These results prompted us to synthesize and study the homologous series of **2**, **4**, and **6**. Although the analogues **1/2**, **3/4**, and **5/6** look similar, they have an important difference in the attachment of amide moieties. In **1**, **3**, and **5**, the phenyl/pyridyl groups are attached to the C-terminal of amide, whereas in **2**, **4**, and **6**, they are attached to the N-terminal of amide. The analogues **2**, **4**, and **6**, can be termed as reverse amides of **1**, **3**, and **5**,

respectively. We have synthesized these reverse amides and crystallized them. The crystal structures were determined, and we analyzed their structures to understand the following aspects.
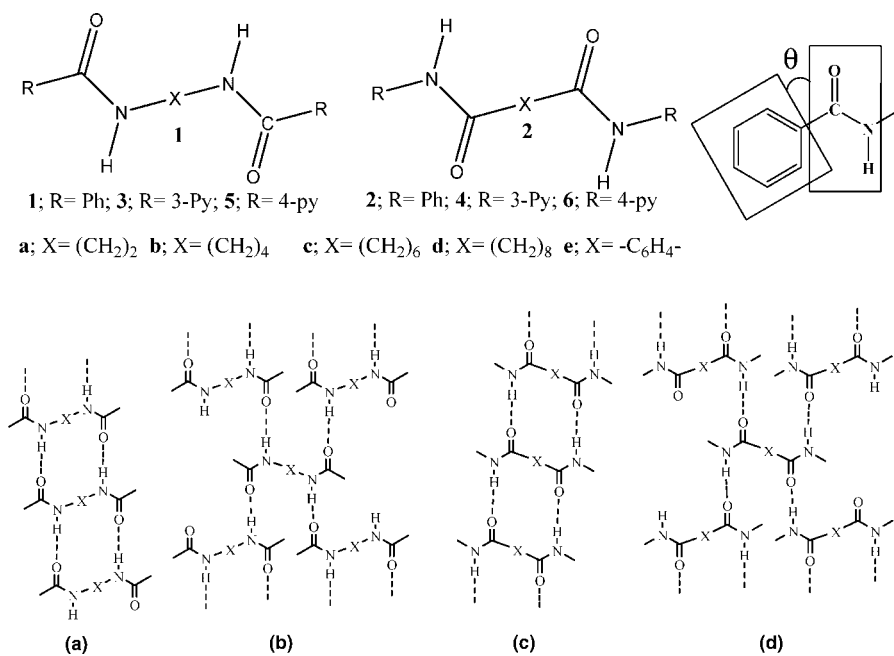
1. Do the reverse amides and amides exhibit iso-structural synthons, in particular, when R and X groups are identical?

2. Does the pyridine group in **4** and **6** interfere in amide-to-amide hydrogen bonds?

3. Do the reverse amides show the dependency on the interplanar angle between amide and pyridine groups in the formation of amide-to-amide hydrogen bonds?

4. Do the homologues exhibit iso-structurality?

5. Do the reverse amides form similar β-sheet and 2D layers.

Results and Discussion

We have employed three well-known synthetic procedures for the preparation of these new compounds. The first method is a one-pot synthesis: reaction of corresponding diacid and amine in the presence of triphenylphosphite and pyridine.[8] Meanwhile, the second method is a two-step procedure: preparation of diester and treatment of the diester with corresponding amine.[9] The third procedure is the preparation of acid chloride and reaction of it with the corresponding amine. The crystallographic parameters for all the crystal structures were given in Table 1.

The crystal structures of **2a**, **2b**, and **2e** were already reported in the literature, and their coordinates were taken from the database for comparative analysis.[10–12] The compounds **2c**, **2d**, **4a–4e** and **6a–6e** were prepared and crystallized in different solvents. Crystals suitable for single crystal analysis were obtained in case of **2c**, **4a–4e**, and **6a–6d**. In this paper, the crystal structures of the reverse amides **2**, **4**, and **6** will be analyzed in comparison with those of **1**, **3**, and **5**. The crystallographic and hydrogen bonding

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Scheme 1. Hydrogen Bonding Patterns: (a) β-Sheet and (b) 2D Layers in Amides and (c) β-Sheet and (d) 2D Layers in Reverse Amides

1; R= Ph; **3**; R= 3-Py; **5**; R= 4-py   **2**; R= Ph; **4**; R= 3-Py; **6**; R= 4-py

a; X= (CH$_2$)$_2$ **b**; X= (CH$_2$)$_4$ **c**; X= (CH$_2$)$_6$ **d**; X= (CH$_2$)$_8$ **e**; X= -C$_6$H$_4$-

(a)   (b)   (c)   (d)

Table 1. Crystallographic Parameters for Compounds 2c–6d

compound	2c	4a	4b	4c	4d	4e	6a	6b	6c	6d
formula	C$_{20}$H$_{24}$N$_2$O$_2$	C$_{14}$H$_{14}$N$_4$O$_2$	C$_{16}$H$_{18}$N$_4$O$_2$	C$_{18}$H$_{22}$N$_4$O$_2$	C$_{20}$H$_{26}$N$_4$O$_2$	C$_{18}$H$_{14}$N$_4$O$_2$	C$_{14}$H$_{16}$N$_4$O$_4$	C$_{16}$H$_{18}$N$_4$O$_2$	C$_{18}$H$_{26}$N$_4$O$_2$	C$_{20}$H$_{30}$N$_4$O$_4$
mol wt	324.41	270.29	298.34	326.40	354.45	318.33	304.31	298.34	362.43	390.48
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	trigonal	monoclinic	orthorhombic
space group	$P2(1)/c$	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P3(2)21$	$P2(1)/n$	$Pbca$
a (Å)	12.402(3)	7.7370(15)	9.4840(19)	8.2247(16)	4.8241(10)	5.2550(11)	6.9253(14)	8.6286(12)	11.694(2)	11.378(2)
b (Å)	5.1053(10)	8.1290(16)	7.7720(16)	9.6843(19)	8.2326(16)	21.051(4)	16.063(3)	8.6286(12)	11.655(2)	16.380(3)
c (Å)	14.286(3)	10.546(2)	10.702(2)	21.939(4)	24.212(5)	6.8150(14)	6.8924(14)	17.727(4)	15.421(3)	22.925(3)
α (deg)	90.00	90.00	90.00	96.00(3)	93.71(3)	90.00	90.00	90.00	90.00	90.00
β (deg)	109.84(3)	102.05(3)	108.21(3)	96.18(3)	96.00(3)	106.62(3)	107.39(3)	90.00	109.33(3)	90.00
γ (deg)	90.00	90.00	90.00	105.83(3)	105.71(3)	90.00	90.00	120.00	90.00	90.00
Vol. (Å^3)	850.9(3)	648.7(2)	749.4(3)	1654.9(6)	917.9(3)	722.4(3)	731.7(3)	1143.0(3)	1983.3(7)	4272.7(15)
Z	2	2	2	4	2	2	2	3	4	8
D_{calc} (Mg/m^3)	1.266	1.384	1.322	1.310	1.282	1.464	1.381	1.300	1.214	1.214
R_1 ($I > 2\sigma(I)$)	0.0505	0.0461	0.0437	0.0560	0.0623	0.0683	0.0547	0.0758	0.0760	0.0725
wR_2 (on F^2, all data)	0.1496	0.1390	0.1450	0.1479	0.2067	0.1838	0.1764	0.2103	0.3111	0.2319

parameters for all the crystal structures were given in Table 1 and Table 2, respectively.

The reported compounds **2a** and **2e** exhibit a β-sheet via N−H···O hydrogen bonds in their crystal structures (Figure 1). Similar to these compounds, the molecules **2c** are also found to assemble via N−H···O hydrogen bonds to form a β-sheet. In contrast, the crystal structure of **2b** is found to contain no β-sheet but a 2D layer via N−H···O hydrogen bonds. Here it is important to note that **1a** and **1b** exhibit a 2D layer while **1c**, **1d**, and **1e** exhibit a β-sheet.[7] These results show that, in case of **1c/2c** and **1e/2e**, the structures exhibit similar supramolecular patterns in both amides and reverse amides. The compound **2d** has been synthesized by us but has been unsuccessful in obtaining crystals suitable for single crystal X-ray diffraction.

Our previous studies on analogues of **3** (R = 3-pyridyl) have shown that **3c**, **3d**, and **3e** form a β-sheet while **3b** forms a 2D network which is doubly interpenetrated in a parallel fashion.[7] However, in the reverse analogues, **4**, the formation of a β-sheet or amide-to-amide hydrogen bonds was not observed. The crystal structures **4a** and **4b** were found to have similar supramolecular architectures via N−H···N

hydrogen bonds (Figure 2). The asymmetric unit of **4a** and **4b** contained only half of the molecule. The alkyl chains in both cases exhibit a perfect anti geometry. In both structures, amide-to-amide hydrogen bonds are not observed as the amide N−H is involved in N−H···N hydrogen bonds with pyridine nitrogen. The molecules form a corrugated 2D layer via N−H···N hydrogen bonds. The amide CO group is involved in C−H···O hydrogen bonds with neighboring layers. Further, both compounds have the θ value of 0° which may be inhibiting the formation of amide-to-amide hydrogen bonds (see Table 3).

It is interesting to note here that the amide **3b** and reverse amide **4b** which have the same R group (3-pyridyl) and spacer X (butyl) have formed 2D layers with identical topology. However, in **3b**, the 2D layer was constituted via amide-to-amide N−H···O hydrogen bonds and also the layers are doubly interpenetrated.

The crystal structures of **4c** and **4d** are found to form iso-structural patterns. The asymmetric unit of **4c** contains two molecules of **4c** while that of **4d** contains one molecule of **4d**. In **4c**, the difference between the two molecules is the value of θ. One molecule has the θ values of 33.4° and 26.5° whereas

**Table 2. Geometrical Parameters of Hydrogen Bonds in Compounds 4 and 6**

	type	H···A (Å)	D···A (Å)	D−H···A (°)
2c	N(21)−H(21)···O(21)	2.16	3.004(3)	167
4a	N(2)−H(2)···N(1)	2.10	2.946(2)	168
	C(4)−H(4)···O(6)	2.62	3.271(3)	128
4b	N(2)−H(2)···N(1)	2.12	2.976(2)	177
	C(4)−H(4)···O(6)	2.89	3.657(3)	141
4c	N(12A)−H(12A)···N(21B)	2.20	3.052(4)	171
	N(12B)−H(12C)···N(21A)	2.16	3.020(4)	173
	N(22A)−H(22A)···O(31A)	2.19	3.026(4)	163
	N(22B)−H(22C)···O(31B)	2.30	3.103(4)	156
	C(34B)−H(34C)···O(38A)	2.72	3.566(5)	146
	C(37B)−H(37D)···O(38A)	2.69	3.546(5)	147
	C(37A)−H(37B)···O(38B)	2.66	3.559(5)	155
	C(34A)−H(34A)···O(38B)	2.75	3.580(5)	144
	C(13B)−H(13B)···N(11A)	2.57	3.347(4)	142
	C(14A)−H(14A)···N(11B)	2.66	3.430(5)	140
4d	N(12)−H(12)···O(29)	2.27	3.076(4)	156
	N(32)−H(32)···N(11)	2.17	3.030(4)	173
	C(26)−H(26B)···O(20)	2.68	3.560(5)	150
	C(21)−H(21A)···O(20)	2.65	3.511(5)	148
	C(34A)−H(34A)···N(31A)	1.92	2.723(9)	143
	C(36)−H(36)···N(31)	2.52	3.339(7)	146
4e	N(12)−H(12)···O(16)	2.29	3.126(4)	165
6a	N(2)−H(2)···O(1W)	1.98	2.839(3)	175
	O(1W)−H···O(1)		2.852(3)	
	O(1W)−H···N(1)		2.878(3)	
6b	N(12)−H(12)···N(11)	2.12	2.940(7)	159
	C(11)−H(11)···O(21)	2.57	3.416(9)	151
	C(22)−H(22B)···N(11)	2.56	3.379(9)	142
6c	N(12)−H(12)···O(2W)	1.95	2.804(6)	174
	N(22)−H(22)···O(1W)	1.99	2.845(4)	170
	O(1W)−H···N(21)		2.827(6)	
	O(2W)−H···N(11)		2.770(6)	
	O(1W)−H···O(1)		2.817(6)	
	O(2W)−H···O(8)		2.788(6)	
6d	N(10)−H(10)···O(2W)	2.08	2.933(4)	174
	N(20)−H(20)···O(1W)	2.02	2.875(5)	173
	O(1W)−H···N(11)		2.835(4)	
	O(2W)−H···N(21)		2.776(4)	
	O(1W)−H···O(30)		2.883(5)	
	O(2W)−H···O(39)		3.010(4)	

the other has 27.9° and 4.3°. In **4d**, this difference has been managed through the disorder of the 3-pyridyl moiety in two positions. Both structures have a similar H-bonding pattern which is somewhat different from the conventional β-sheet (Figure 3). Conventionally, the β-sheet contains all N−H···O hydrogen bonds, whereas in the structures observed here, it contains N−H···O as well as N−H···N hydrogen bonds. The N−H···O dimeric motif and N−H···N dimeric motif alternate in the new β-sheet. Therefore, partial interference of the pyridine group in the amide-to-amide hydrogen bond occurred in these structures. The pyridine group and C=O group which are not involved in strong hydrogen bonds involve in C−H···N and C−H···O hydrogen bonds, respectively. Here, it is interesting to note that the analogues of **1** (**1c** and **1d**) and **3** (**3c** and **3d**) exhibited conventional β-sheet patterns. Therefore, unlike in amides **3c** and **3d**, the 3-pyridyl groups in reverse amides (**4c** and **4d**) have shown an interference in amide-to-amide hydrogen bonds.

Among the analogues of **4**, **4e** is the unique example as it forms a similar β-sheet pattern as the amide **3e** (Figure 4). It is noteworthy that compound **1e** has been crystallized in two polymorphic forms. One of the polymorphs contains the β-sheet network similar to **3e** or **4e**, while the other has a 2D layer.[13,14] Although **4e** contains a similar β-sheet pattern as **3e**, the structure **4e** is not iso-structural to **3e** due to the differences in the arrangement of β-sheets with respect to each other. For example, in **4e**, the pyridyl N-atoms were not engaged in any significant hydrogen bonding interactions with C−H groups. The shortest C−H···N interaction contains the geometrical parameters of C···N 3.244 Å, H···N 3.168 Å, and C−H···N 86.3°. The H···N and C−H···N values deviate from those of a proper contact. In fact, the pyridine groups in **4e** interact with each other via edge-to-face aromatic interactions, and hence, there are short C···N distances. Meanwhile, in **3e**, the pyridyl groups form C−H···N dimeric synthons which join the β-sheets.
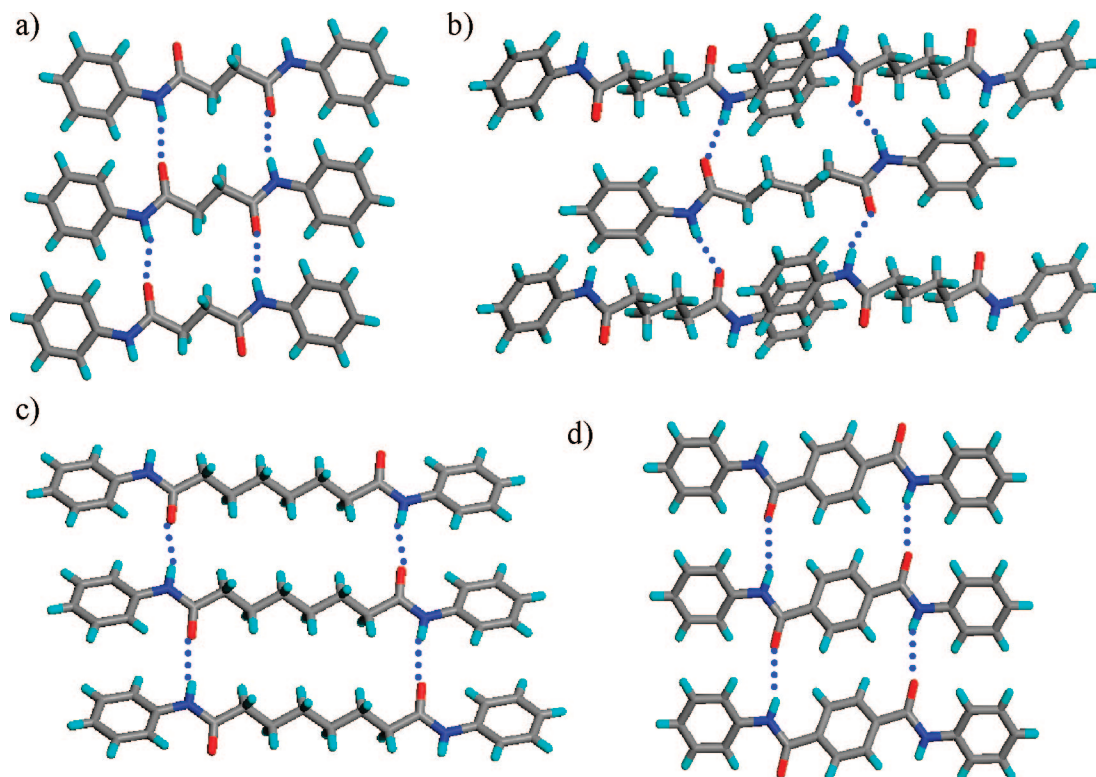
Figure 1. Hydrogen bonding patterns in the crystal structures of (a) **2a** (β-sheet); (b) **2b** (2D layer); (c) **2c** (β-sheet); and (d) **2e** (β-sheet).
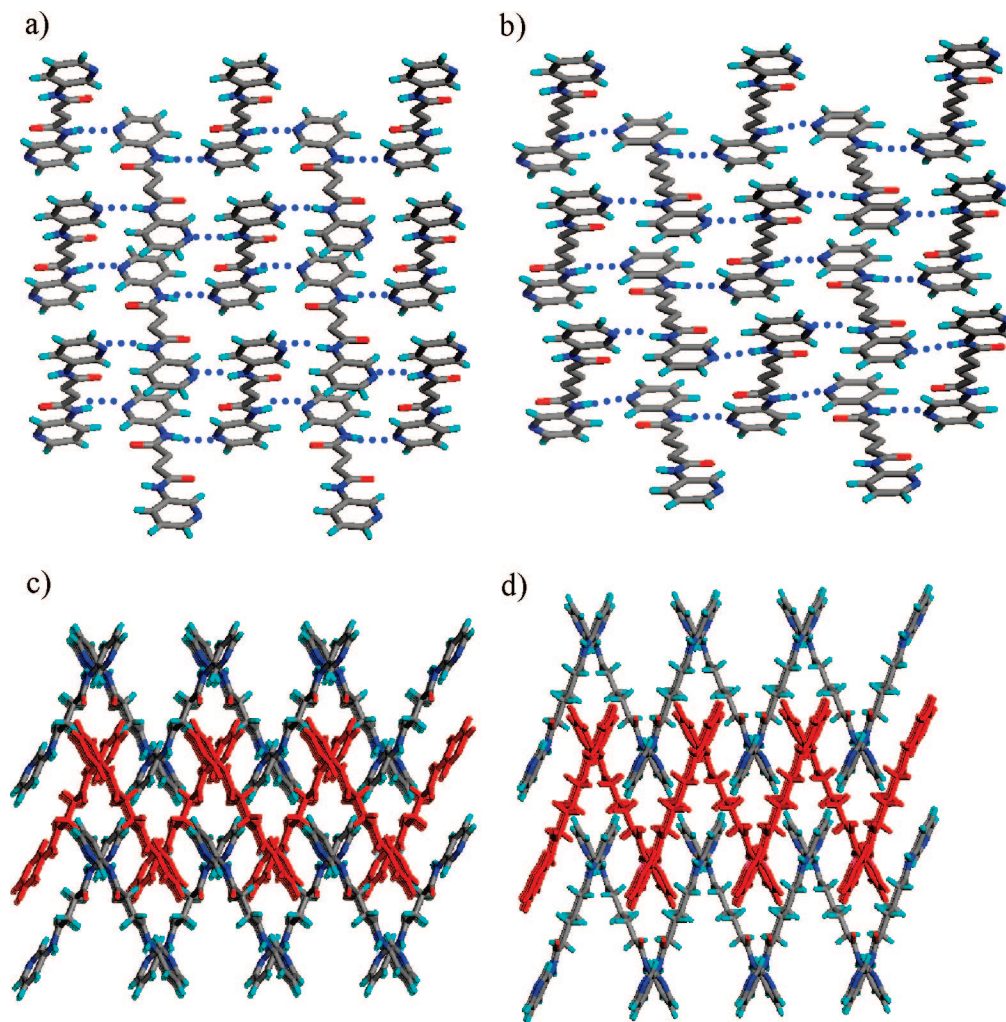
Figure 2. Illustrations for the crystal structures of **4a** and **4b**: 2D layers via N–H···N hydrogen bonds in (a) **4a** and (b) **4b**; packing of 2D layers in (c) **4a** and (d) **4b**. For the sake of clarity, the central layers were colored in red.

**Table 3. Values of θ in the Crystal Structures of 1–6**

|	a	b	c	d	e
2	34.6°	26.6°	34.7°	*a*	28.4°
4	0°	0°	33.4 and 26.5° 27.9 and 4.3°	35 and 29.6° 25.8 and 23°	30.4°
6	1.4°	7.2°	1.1 and 7.3°	6.5 and 5.0°	*a*
1	19°	30.0°	29.3°	29.2°	29 and 24°
3	*a*	20.7°	26.4°	26.8°	29.4°
5	11.9°	29.4°	29.5°	29.3°	*a*

a Crystal structures are not determined.

In total contrast to the above results, the analogues of **6** have exhibited very different structures from the rest of the lot. The compounds **6a**, **6c**, and **6d** are the first examples for the inclusion of water in the crystal lattice among the derivatives **1**−**6**. Therefore, the hydrogen bonding patterns observed in these structures cannot be compared with those observed in the structures **1**−**5**. All three structures contain two water molecules per formula unit. The compounds **6c** and **6d** are found to have similar supramolecular geometries, while **6a** exhibits a different structure (Figure 5). The crystal structure **6a** contains one water molecule and a half-unit of molecule **6a** in the asymmetric unit. Indeed, this β-sheet-like pattern was observed in this structure but amide N−H and C=O groups are joined via water molecules. Each water molecule is engaged in three hydrogen bonds: one each with amide CO, pyridine N-atom, and amide N−H. The water molecules join these sheets into 3D layers.

In the crystal structures of **6c** and **6d**, the asymmetric units contain one molecule of **6c** or **6d** and two water molecules. The molecule does not have a linear geometry as one of the torsion angles ((H)N−C(O)−C−C) is not close to 180° (93° in **6c** and 89° in **6d**). The alkyl chain exhibits all anti conformations in **6c**, while in **6d** there are two gauche conformations with the C−C−C−C torsions of 93° and 78° (Figure 6). In both cases, water molecules join these molecules such that there is formation of a tubular structure.

The crystal structure of **6b** happened to be highly unpredictable and unprecedented. The compound **6b** is crystallized in trigonal space group *P*3$_2$21, and an asymmetric unit contains half of the molecule **6b** (Figure 7). The butyl chain exhibits an anti−gauche−anti conformation with the torsion values of 176.6° and 71.6°. As a result, the molecule is not linear and exhibits an arclike geometry (Figure 7a). In the crystal structure, the amide N−H group and pyridine groups are engaged in N−H···N hydrogen bonds to form a 3D network. The 3D network has been formed due to the linking of the molecules in a helical fashion via N−H···N hydrogen bonds (Figure 7e) and also due to the fact that the ligand exhibits the geometry of a 4-connected node. The nonplanarity of the molecule transforms the molecule into a nonplanar 4-connected node which is formed by two pyridine groups and two N−H groups (Figure 7b). These nodes join together to form a network
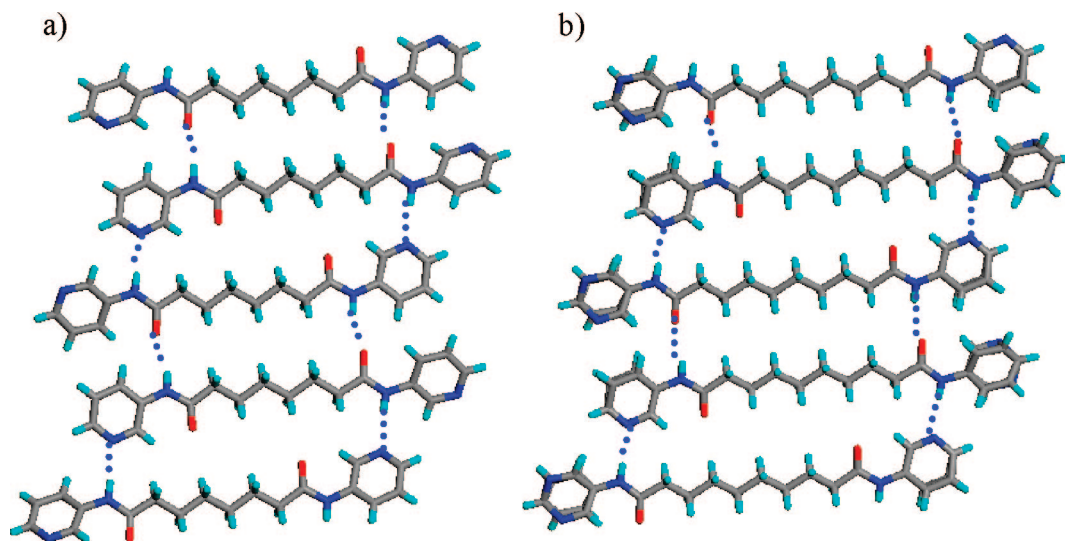
Figure 3. Hydrogen bonding patterns in the crystal structures of (a) **4c** and (b) **4d**. The 3-pyridyl rings are disordered.
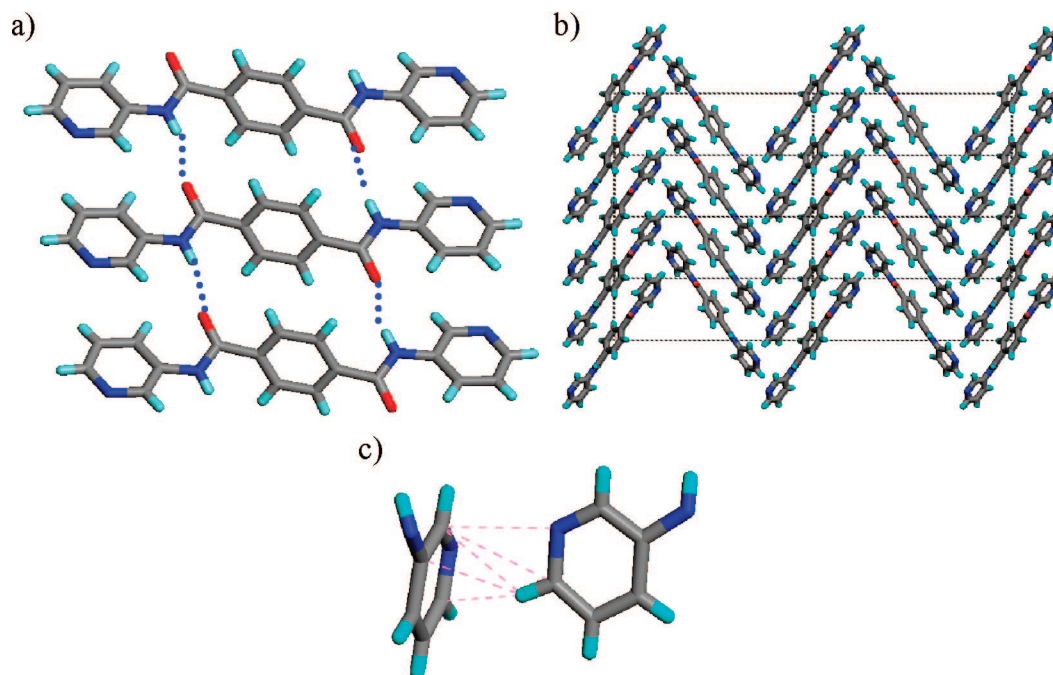
Figure 4. Illustrations for the crystal structure of **4e**: (a) β-sheet; (b) packing diagram; (c) edge-to-face aromatic interactions. The dotted lines represent the contacts within the distance range of 2.8 to 3.4 Å.

containing a quartzlike geometry which is denoted by Wells as $6^4 8^2$-b (Figure 7c and d).[15]

To our knowledge, this is the first example of a quartz network in pure organic materials. In the case of metal–organic networks, few examples containing a quartz topology have been reported in the literature.[16] The major difference between the quartz network and the one observed here is that hexagonal helices of the quartz network are distorted in **6b** to give rise to the trigonal symmetry. Similar distortion was noted in the structure of {Co(4,4′-dicarboxy-2,2′-bipyridine)(H$_2$O)$_2$}$_n$.[17] However, in that complex, networks exhibit 2-fold interpenetration, whereas in 6b the networks exhibit 4-fold interpenetration. We note here that the 4-fold interpenetration of networks containing quartz topology is unprecedented.

The powder X-ray diffraction patterns of the missing reverse amides **2d** and **6e** were recorded as crystals suitable for single

crystal X-ray analyses were not obtained. These spectra indicate that crystal structures of **2d** and **6e** may have similar features as those of **2c** and **4e**, respectively.

Conclusions

These studies show that reverse amides are somewhat isostructural when R is phenyl, two out of four. However, when R is pyridyl, the interference of the pyridine group in amide-to-amide hydrogen bonds is found to be greater in reverse amides. For example, in 3-pyridyl derivatives, the pyridine group interfered in amide-to-amide hydrogen bonds in four structures out of the five reported here. The structures of reverse amides containing 4-pyridine units seem to be very different from the rest of the five analogues. Out of four structures reported here, three include water molecules and one forms an unexpected but novel network with quartz topology. From the θ values of compounds containing
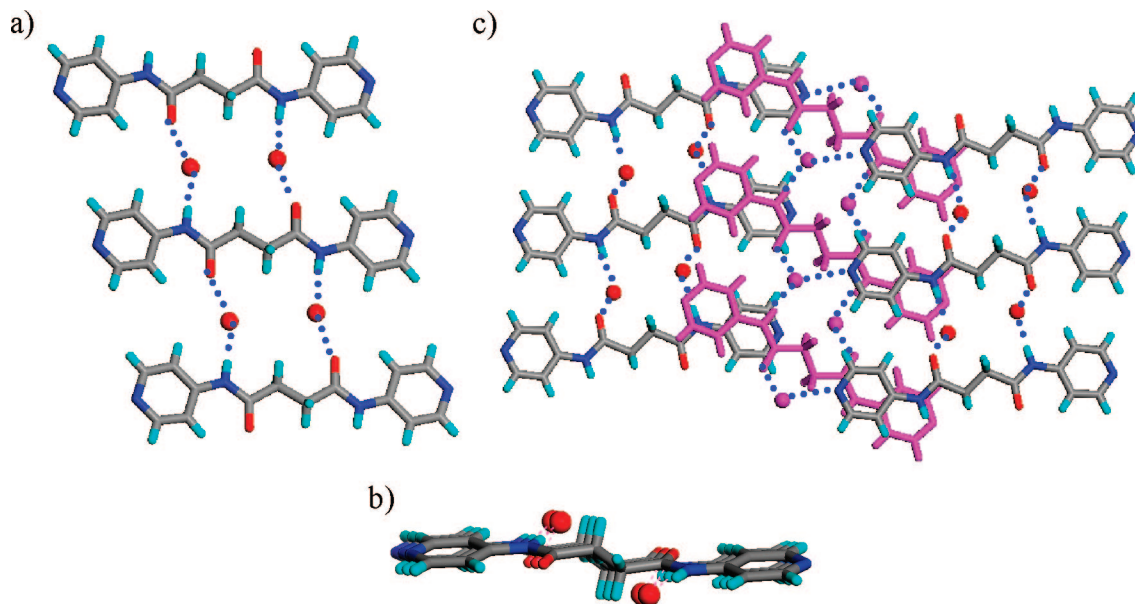
Figure 5. Illustrations for the crystal structure of **6a**: (a) β-sheet-like motif formed via water molecules; (b) side view of the layer; (c) packing of the β-sheets into 3D layers.
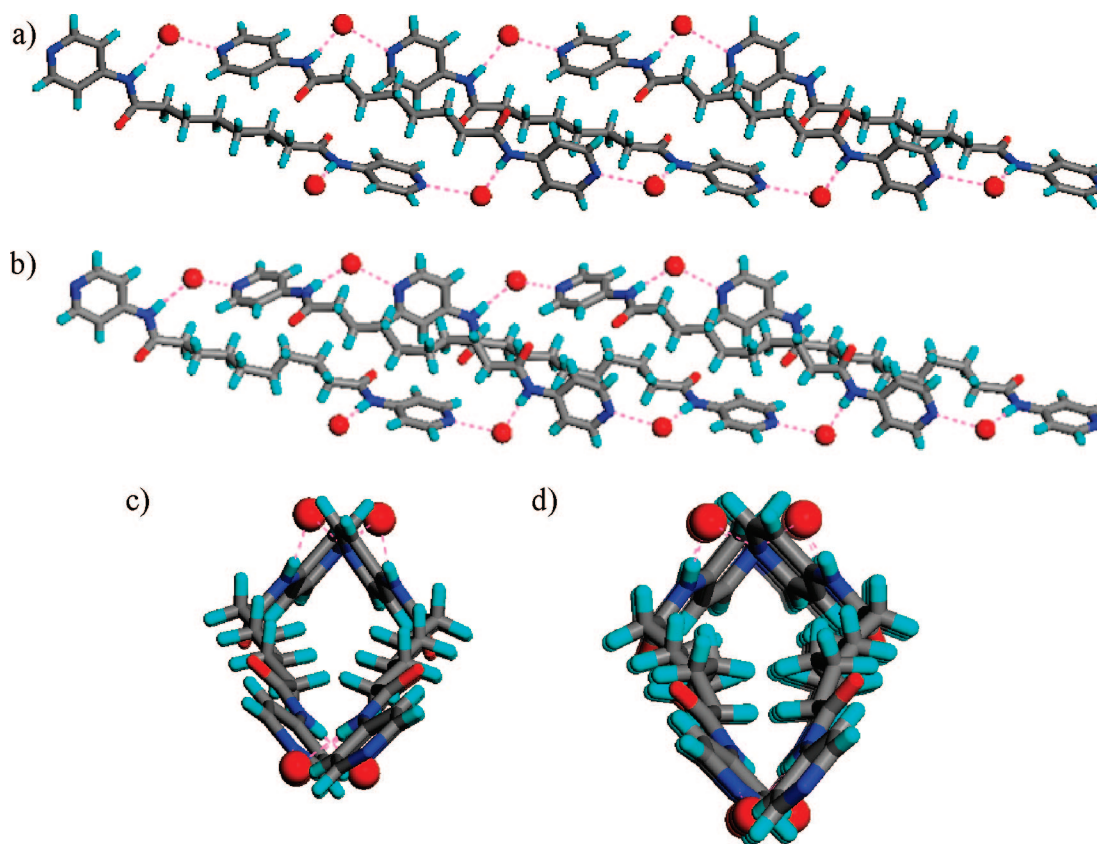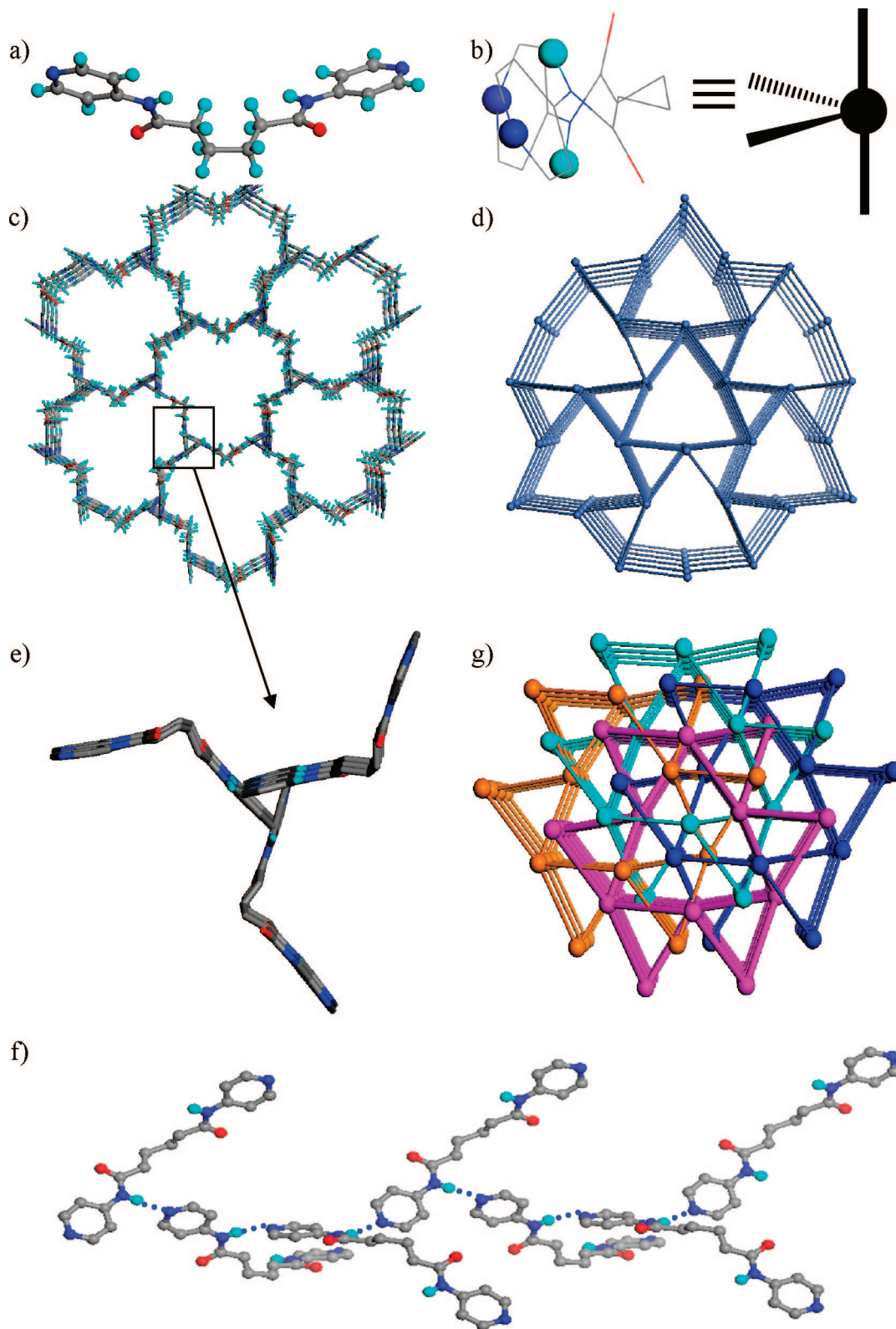

Figure 6. Illustrations for the crystal structures **6c** and **6d**: tubular structures observed in (a) **6c** and (b) **6d**; top view of the tubes in (c) **6c** and **6d**.

pyridines, it can be observed that the reverse amides (**4** and **6**) exhibit values less than 7° in six compounds out of nine, whereas in amides (**3** and **5**) the θ value is less than 19° in only one compound out of eight. Accordingly, only three compounds of **4** and **6** exhibit amide-to-amide hydrogen bonds, whereas seven compounds of **3** and **5** form amide-to-amide hydrogen bonds out of eight compounds. These studies show that the amides and reverse amides which have same spacer X and R may not necessarily be iso-structural in particular when R group has the ability to form hydrogen bonds with amide functionalities.

Experimental

Initially, we tried to prepare all the compounds through a one-step synthesis by reacting diacid and amine in the presence of triphenylphosphite and pyridine. However, this procedure failed to form the products in the case of 4-amino pyridines. Therefore, for the reactions containing 4-aminopyridines, the ester and acid chloride procedures were employed.

Figure 7. Illustrations for the crystal structure of **6b**: (a) arc-shaped geometry of the ligand; (b) geometry of the node for network formation; (c) network with quartz topology; (d) network when the molecules are reduced to nodes and 3-fold helix via N−H···N hydrogen bonds; (e) top view and (f) side view; (g) 4-fold interpenetration of quartz networks.

Procedure for the Synthesis of 2c−d and 4a−e. 3-Amino pyridine or aniline (2 mmol) was added to 40 mL of a pyridine solution of dicarboxylic acid (1 mmol), and the solution was stirred for 15 min. To this solution was added triphenyl phosphite (2 mmol), and the mixture was refluxed for 5 h. The volume of the solution was reduced to 5 mL by distilling out the pyridine, and a white precipitate was obtained. The solid was filtered, washed with water, and dried under vacuum.

(**2c**) Yield: 90.39%. Mp: 180–184 °C.
(**2d**) Yield: 80.45%. Mp: 160–163 °C.
(**4a**) Yield: 75.00%. Mp: 196–200 °C.

(**4b**) Yield: 65.00%. Mp: 216–220 °C.
(**4c**) Yield: 88.81%. Mp: 190–193 °C.
(**4d**) Yield: 54.28%. Mp: 182–185 °C.
(**4e**) Yield: 72.00%. Mp: 216–218 °C.

Procedure for the Synthesis of 6b, 6c, and 6d. 4-Amino pyridine (2 mmol) and TEA (2.5 mmol) in tetrahydrofuran (THF) was cooled to 0 °C, and to it was added the corresponding dicarboxylic−acid chloride (1 mmol) dropwise with continuous stirring .The solution was stirred overnight. The solid was filtered, washed with water, and dried under vacuum.

(**6b**) Yield: 67.78%. Mp: 158–162 °C.
(**6c**) Yield: 78.50%. Mp: 183–187 °C.
(**6d**) Yield: 69.80%. Mp: 146–150 °C.

Procedure for the Synthesis of 6a. Preparation of the Methyl Ester of Succinic Acid. To the stirred suspension of succinic acid (2 g, 0.0169 M) in dry MeOH (60 mL) at 0 °C, freshly distilled thionyl chloride (20.16 g, 0.1694 M) was added dropwise. The resulting turbid solution was stirred for 2 h and then refluxed for 3 h. Excess MeOH and SOCl$_2$ were distilled off from the resulting clear solution. The yellow oil was suspended in 60 mL of Et$_2$O at 0 °C, and a 50 mL solution of saturated NaHCO$_3$ was slowly added. After stirring continued for 1 h, the organic layer was removed and the aqueous layer was extracted by Et$_2$O (5 × 30 mL). The organic extracts were combined and dried over K$_2$CO$_3$. The ether was distilled off to get the methyl ester of succinic acid (yellow liquid). Yield: 55.12%.

Procedure for the Synthesis of 6a from the Methyl Ester of Succinic Acid. Freshly distilled DMSO (30 mL), NaH (1.9725 g, 0.0822 M), and 4-amino pyridine (3.8679 g, 0.0411 M) were placed in a two-neck flask under an inert atmosphere, and the mixture was cooled to 0 °C. The dry DMSO solution (10 mL) of the diester of succinic acid (2.0 g, 0.0136 M) was added dropwise to the above solution. After 15 h of continuous stirring at room temperature, the resulting brown solution was poured into cracked ice under vigorous stirring. The white solid that precipitated out after 20 min was filtered and washed with water several times and finally with acetone. Yield: 69.90%. Mp: 206–208 °C.

Synthesis of 6e. Preparation of the Methyl Ester of Terephthalic Acid. To the stirred suspension of terephthalic acid (2 g, 0.0120 M) in dry MeOH (40 mL), conc H$_2$SO$_4$ (5.9035 g, 0.0602 M) was added dropwise. The resulting solution was refluxed for 12 h. Excess MeOH was distilled off from the resulting clear solution. The resulting white solid is worked up in a similar way to that of the diester of succinic acid, and a white solid of the diester of terphthalic acid in 45.25% yield was obtained.

Procedure for the Synthesis of 6e. The compound **6e** was prepared by employing a similar procedure to that of the synthesis of **6a** from ester. Yield: 32.47%. Mp: >300 °C.

Crystal Structure Determination. The single crystal data for all the structures were collected on a Bruker-Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ-scan method). The structures were solved by direct methods and refined by least-squares methods on F^2 using SHELX-97.[18] Non-hydrogen atoms were refined anisotropically, and H-atoms were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding parental atoms. The fractional coordinates, full list of bond lengths and angles, and the anisotropic displacement parameters are available in the Supporting Information. Pertinent crystallographic details were given in Table 1, and hydrogen bond details were given Table 2. In compound **6d**, the pyridyl groups exhibit disorder which has been modeled and refined.
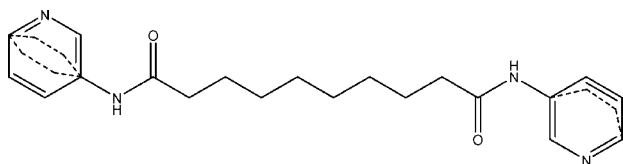
Supporting Information Available: (1) Crystallization experiments, (2) elemental analysis, (3) IR spectra, (4) experimental and calculated XRPD spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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