

## Hydrogen-Bonding Motifs in the Crystals of Secondary Diamides with 2-Amino-6-methyl- and 2,6-Diaminopyridine Subunits

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Received 22 July 1999; accepted 3 September 1999

**Abstract:** Hydrogen-bonding motifs in the crystal structures of *N,N*-bis-(6-methyl-pyridin-2-yl)-isophthalamide (1), 1,3-bis[[6-methyl-pyridin-2-yl)amino]carbonyl-methoxy]benzene (2), *N,N*-bis-(6-amino-pyridin-2-yl)-isophthalamide (3) and 1,3-bis[[6-amino-pyridin-2-yl)amino]carbonyl-methoxy]benzene (4) are reported. The hydrogen bond preferences were analyzed. © 1999 Elsevier Science Ltd. All rights reserved.

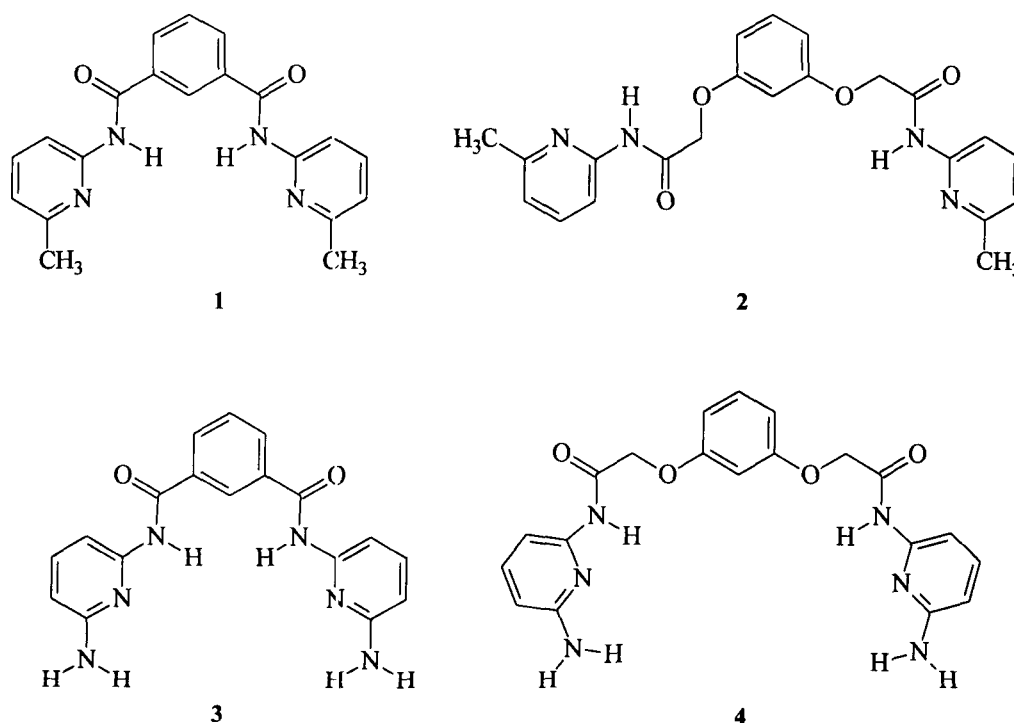
**Keywords:** hydrogen bonding; molecular recognition; self-assembly

Essential to the design of self-assembled materials possessing novel properties is an increased understanding of the solid-state packing. Although the formation of any particular crystal structure is the result of the cooperation of a large number of interactions, making predictions uncertain, the identification and study of biomimetic motifs of weak interactions may well provide some rules for the controlled assembly of supramolecular architectures useful in the design of solids with specific solid-state properties.<sup>1-8</sup> Particularly hydrogen-bonding interactions are a promising approach to the control of solid-state structures.<sup>9-11</sup> Advances in this area are not only likely to facilitate the creation of new useful materials, but also to provide insight into molecular recognition phenomena. Analysis of the crystal structure packing patterns of hydrogen bonded molecules can also give some insight into the formation of well-defined and stable aggregates from small molecular components in solution.<sup>12,13</sup>

This study concerns the preferences of the amide-NH $\cdots$ O=C motif in the crystal structure of secondary diamides in case where competitive acceptor- or/and donor-groups are part of the molecular structure. Our aim is to analyze the hydrogen bond packing of R-NHCO-X-CONH-R as a function of the residue R and the spacer X. In this work the crystal structures of secondary diamides with two 2-amino-6-methyl- and 2,6-diaminopyridine subunits (R = C<sub>5</sub>H<sub>3</sub>N-CH<sub>3</sub>; C<sub>5</sub>H<sub>3</sub>N-NH<sub>2</sub>) linked by a rigid or flexible spacer (X = C<sub>6</sub>H<sub>4</sub>; CH<sub>2</sub>-O-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>2</sub>) are described. The compounds currently under study are *N,N*'-bis-(6-methyl-pyridin-2-yl)-isophthalamide (1), 1,3-bis[[6-methyl-pyridin-2-yl)amino]carbonyl-methoxy]benzene (2), *N,N*'-bis-(6-amino-pyridin-2-yl)-isophthalamide (3) and 1,3-bis[[6-aminopyridin-2-yl)amino]carbonyl-methoxy]benzene (4). This type of molecules has been used as synthetic receptors or as subunits for host structures, which are able to recognize some organic guest molecules.<sup>13-17</sup>

Analysis of the noncovalent interactions determining the crystal structure of these compounds can be helpful for the design of new synthetic receptor molecules containing preorganized subunits, and for the study of host-guest interactions in the solid state.

The molecules of **1** and **2** have two equivalent proton donor groups (two amide-NH), whereas **3** and **4** possess four potential groups of proton donors (two amide NH and two NH<sub>2</sub> groups) available for hydrogen bonding. The aromatic-, methylene- and methyl-hydrogen atoms may act additionally as weak hydrogen bond donors. The potential proton acceptor atoms in **1-4** are two pyridine nitrogens and two amide oxygens, compounds **2** and **4** contain also two ether oxygen atoms.



The compounds **1-4** were prepared by the reaction of 2-amino-6-methylpyridine or 2,6-diaminopyridine with the corresponding diacid chloride, namely isophthaloyl dichloride and *m*-phenylenedioxy-diacetyl chloride. Compound **1** was crystallized from a benzene / ethyl acetate mixture, crystals of **2-4** were obtained by slow evaporation of the solvent from THF / hexane solutions.

X-ray crystallography established that compounds **1**, **3** and **4** form a concave structure in the solid state. Contrary, 1,3-bis[[(6-methyl-pyridin-2-yl)-amino]carbonyl-methoxy]benzene (**2**) exists in an asymmetrical, S-shaped structure. Figure 1 shows the monomeric units of **1-4** in the crystalline state.

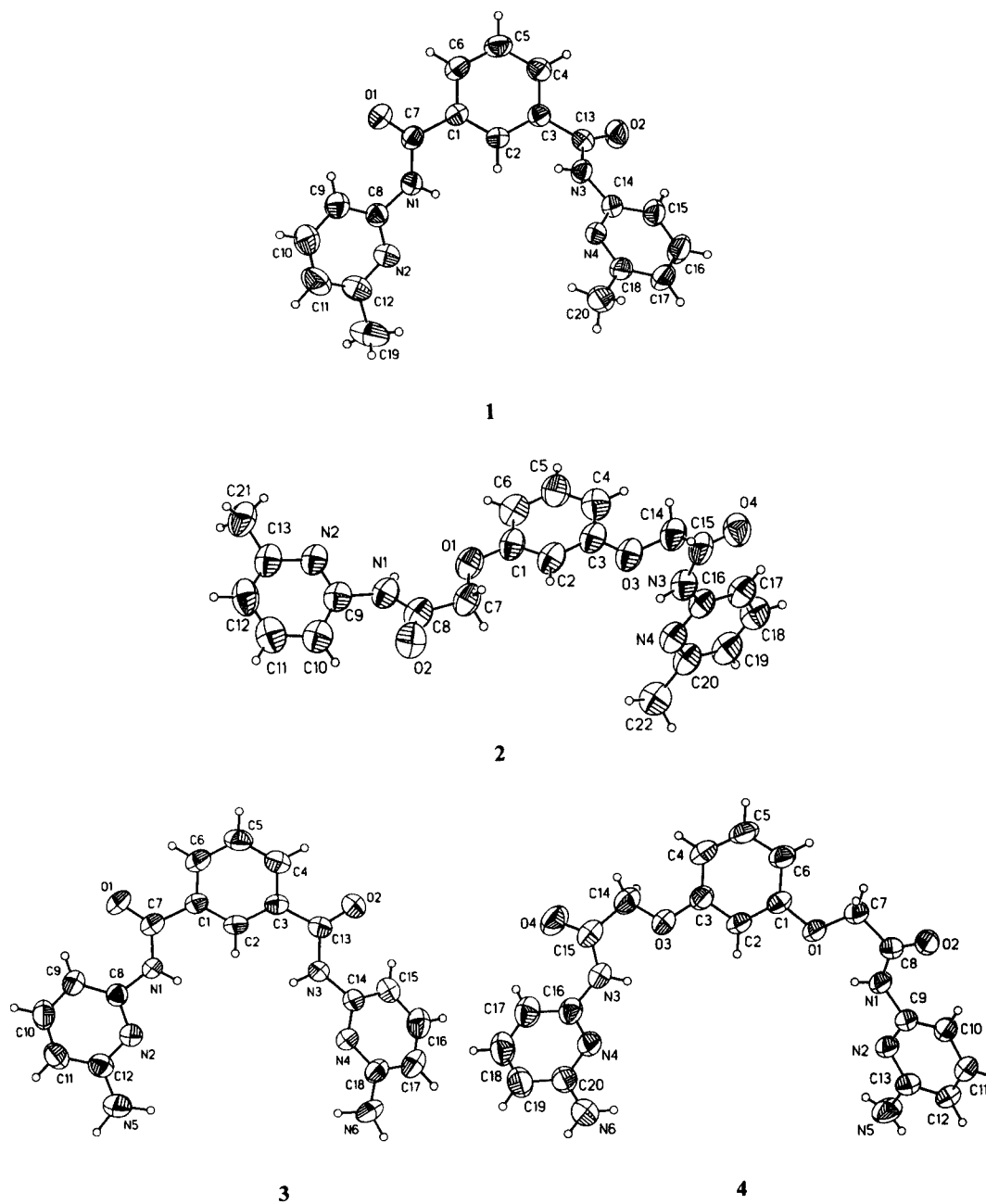


Figure 1. ORTEP drawing of compounds 1-4 showing the monomeric units.

The X-ray structures reveal that *N,N'*-bis-(6-methyl-pyridin-2-yl)-isophthalamide (**1**) exists in the solid state as a NH $\cdots$ N hydrogen-bonded dimer (Figure 2). The dimers interact via stacking interactions between the phenyl rings and CH $\cdots$ O interactions between the phenyl hydrogens and the amide oxygens (Figure 3). The interplanar angles between each pyridine unit and the central benzene ring of **1** are 39.8° and 31.9°, respectively, the interplanar angle between both pyridine rings amounts to 47.5°.

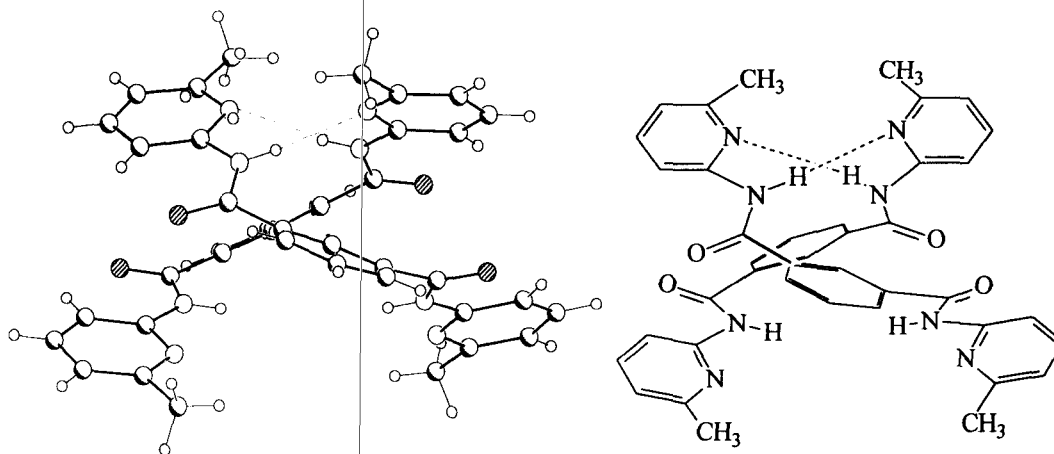
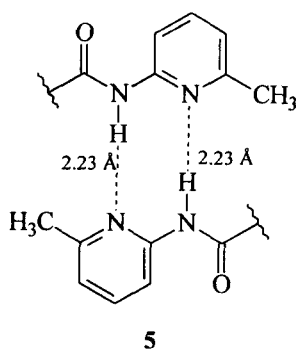


Figure 2. X-ray and schematic structure of the dimer of **1**.

Only one NH proton and one pyridine N atom from each molecule of **1** are used in the hydrogen bonding pattern, corresponding to the motif **5** with bidentate hydrogen bonds. Interactions of NH to the ring nitrogen are preferred over hydrogen bonds to the carbonyl O atom. The distances of amide-NH $\cdots$ N-pyr contacts are 2.23 Å (N $\cdots$ N distance, 3.08 Å; NH $\cdots$ N angle, 175.6°). The intermolecular CH $\cdots$ O contacts have a distance of 2.55 Å (C $\cdots$ O distance, 3.25 Å; CH $\cdots$ O angle, 122°) and 2.78 Å (C $\cdots$ O distance, 3.36 Å; CH $\cdots$ O angle, 113°). Additionally, a water molecule forming a hydrogen bond to the pyridine nitrogen atoms was found.



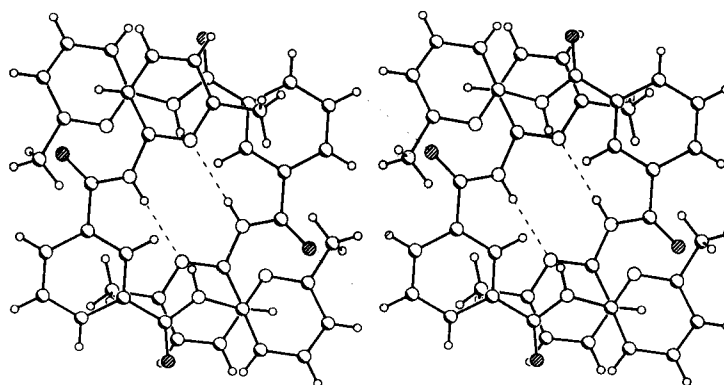


Figure 3. Packing of **1** in the crystal (view down the axis b).

The average molecular weight of the aggregates of **1** was also determined in solution by vapor pressure osmometry at 25 °C in chloroform using benzil as molecular weight standard. These studies indicate that compound **1** dimerizes in chloroform and the average molecular weight even in a saturated solution does not exceed that of the dimer.

1,3-Bis[[[6-methyl-pyridin-2-yl)-amino]carbonyl-methoxy]benzene (**2**) self-assembles into NH $\cdots$ N hydrogen-bonded chains (Figure 4). Both amide NH protons and both ring nitrogens of each molecule are used for hydrogen bonding. Each molecule of **2** is involved in four NH $\cdots$ N hydrogen bonds with distances of 2.26 Å (N $\cdots$ N distance, 3.05 Å; NH $\cdots$ N angle, 153°) and of 2.29 Å (N $\cdots$ N distance, 3.07 Å; NH $\cdots$ N angle, 150.8°). Hydrogen bonds between amide NH and pyridine N are preferred over interactions to the amide-O atom.

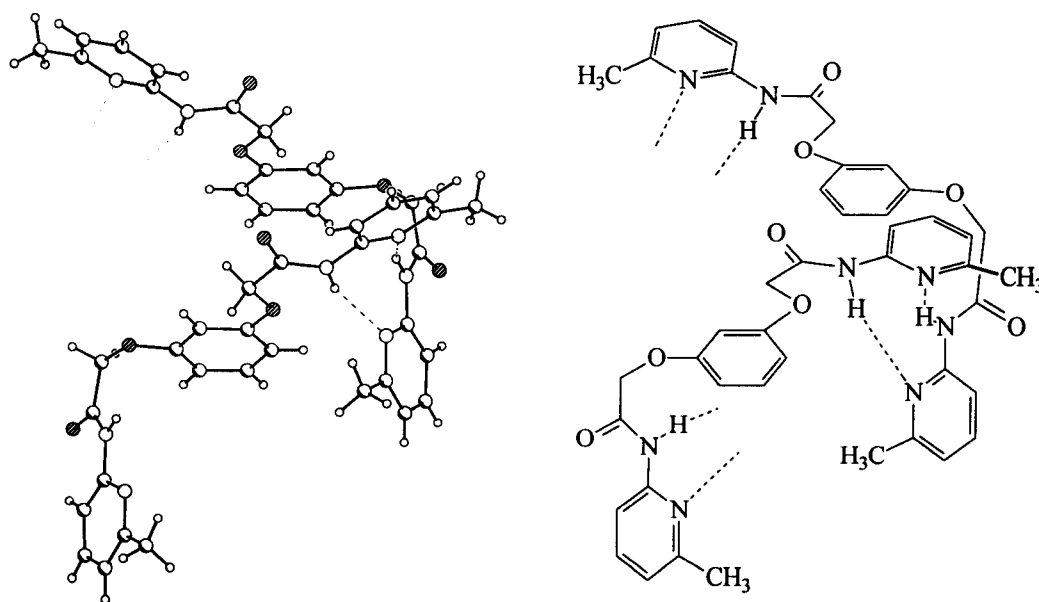
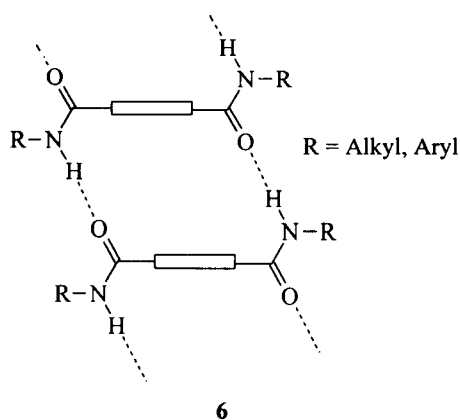


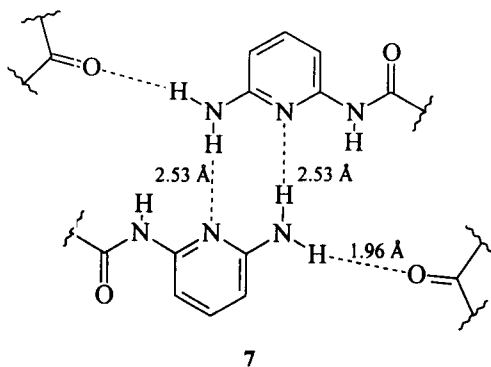
Figure 4. X-ray and schematic structure of the packing of **2**.

The methyl groups and pyridine hydrogen atoms (H11, H18, numbering in Figure 1) participate in short interactions with the amide-O, distances of 2.54 Å ( $\text{H}_2\text{CH}\cdots\text{O}=\text{C}$ ,  $\text{C}\cdots\text{O}$  distance, 3.49 Å;  $\text{CH}\cdots\text{O}$  angle,  $147^\circ$ ) and 2.79 Å ( $\text{pyr-H}\cdots\text{O}=\text{C}$ ,  $\text{C}\cdots\text{O}$  distance, 3.65 Å;  $\text{CH}\cdots\text{N}$  angle,  $136^\circ$ ) are observed. The ether oxygen is not used for hydrogen bonding.

The common hydrogen-bonding pattern typical for secondary diamides, involving amide- $\text{NH}\cdots\text{O}=\text{C}$  contacts, is not present in the crystal structures of 1 and 2. Secondary diamides (for example *N,N'*-diphenylisophthalamide,<sup>18</sup>  $\text{R} = \text{X} = \text{C}_6\text{H}_5$ ) tend to form hydrogen bonds by translation (motif 6).<sup>18-21</sup> In our cases, however, the presence of the pyridine rings change the packing pattern. The molecules now prefer amide- $\text{NH}\cdots\text{N-pyr}$  contacts over amide- $\text{NH}\cdots\text{O}=\text{C}$  interactions.



The presence of the amino groups in structure 3 causes the formation of amine- $\text{NH}\cdots\text{O}=\text{C}$  and amine- $\text{NH}\cdots\text{N-pyr}$  interactions. Compound 3 assembles in a way that the amino group and not the amide NH (as in 1) acts as hydrogen bond donor. Amine- $\text{NH}\cdots\text{O}=\text{C}$  and amine- $\text{NH}\cdots\text{N-pyr}$  contacts have preference over amide- $\text{NH}\cdots\text{X}$  ( $\text{X} = \text{O}, \text{N}$ ) interactions (motif 7). The distances of 2.53 Å for the  $(\text{H})\text{NH}\cdots\text{N}$  contacts ( $\text{N}\cdots\text{N}$  distance, 3.41 Å;  $\text{NH}\cdots\text{N}$  angle,  $142^\circ$ ) and distances of 1.96 Å for the  $(\text{H})\text{NH}\cdots\text{O}$  contacts ( $\text{N}\cdots\text{O}$  distance, 2.93 Å;  $\text{NH}\cdots\text{N}$  angle,  $154^\circ$ ) are observed.



The interplanar angle between the phenyl and the pyridine rings of **3** are 6.5 and 49.6°, the interplanar angle between both pyridine rings is 51.2°. The packing of **3** in the crystal is shown in Figure 5.

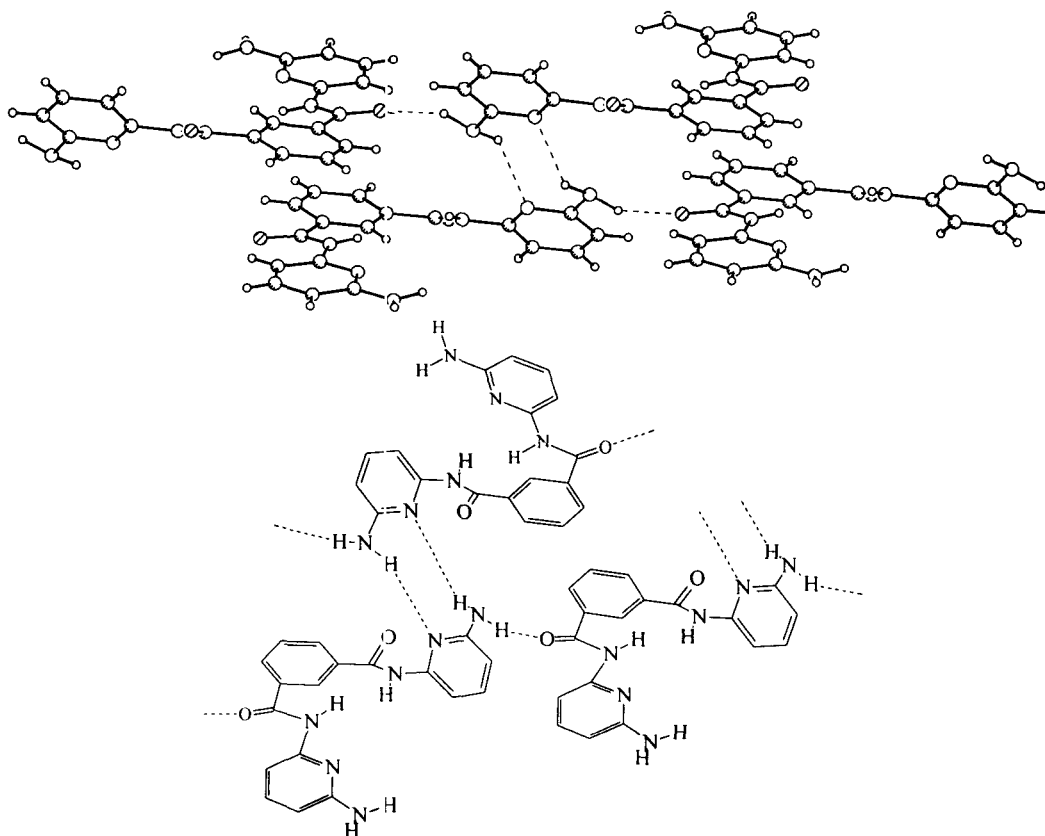
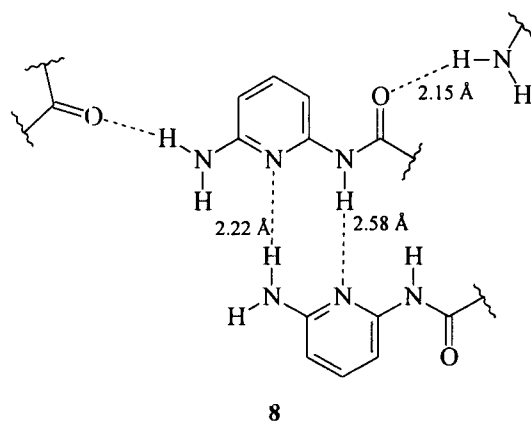


Figure 5. X-ray and schematic structure of the packing of **3**.

X-ray crystallographic analysis of **4** established that all types of proton donors and proton acceptors are used in the hydrogen bonding pattern. Compound **4** crystallizes in space group  $P2_1/c$ . The interplanar angles between phenyl and pyridine rings of **4** are 27.9 and 35.8°, respectively, the interplanar angle between pyridine rings amounts to 122°. Each molecule of **4** participates in two amine-NH $\cdots$ O=C, two amine-NH $\cdots$ N-pyr, and two amide-NH $\cdots$ N-pyr hydrogen bonds. The (H)NH $\cdots$ N contacts with distances of 2.22 Å (N $\cdots$ N distance, 3.08 Å; NH $\cdots$ N angle, 161.7°), (H)NH $\cdots$ O contacts with distances of 2.15 Å (N $\cdots$ O distance, 2.98 Å; NH $\cdots$ O angle, 173.5°) and amide-NH $\cdots$ N contacts with distances of 2.58 Å (N $\cdots$ N distance, 3.41 Å; NH $\cdots$ N angle, 162.7°) are found (motif **8**).



Additionally, the pyridine hydrogens (H11, H18, numbering in Figure 1) participate in short  $\text{CH}\cdots\text{O}$  interactions with the amide oxygens (pyr-H $\cdots\text{O}=\text{C}$  distance, 2.47 Å; C $\cdots\text{O}$  distance, 3.36 Å; CH $\cdots\text{O}$  angle, 139°). The methylene hydrogens form short intermolecular contacts with the ether oxygens (-HCH $\cdots\text{O}-\text{CH}_2-$  distance, 2.62 Å; C $\cdots\text{O}$  distance, 3.50 Å; CH $\cdots\text{O}$  angle, 138°). Figures 6 and 7 show the packing of molecules of **4** in the crystal.

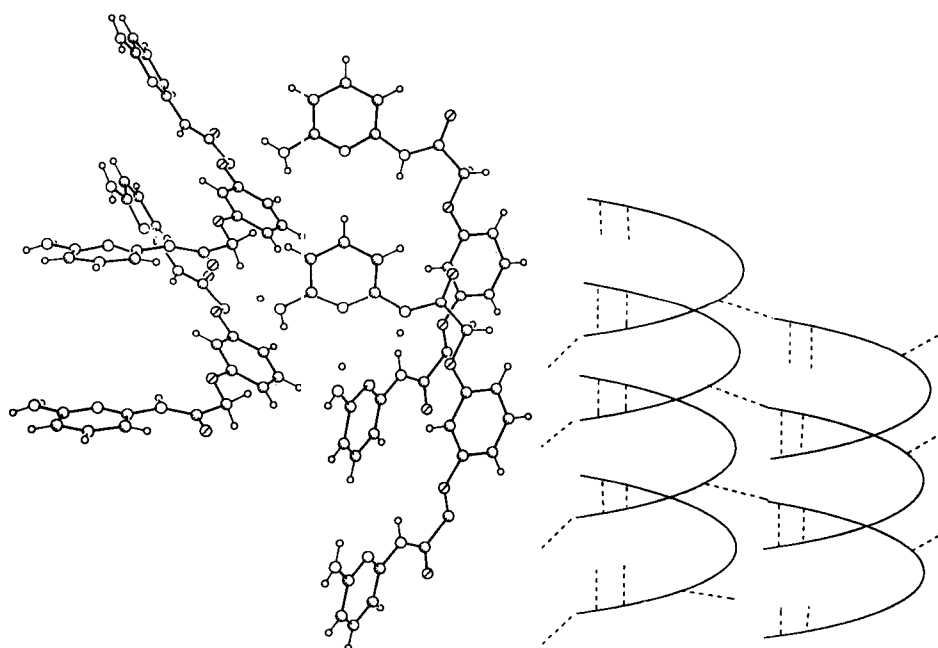


Figure 6. X-ray and schematic structure of the packing of **4**.



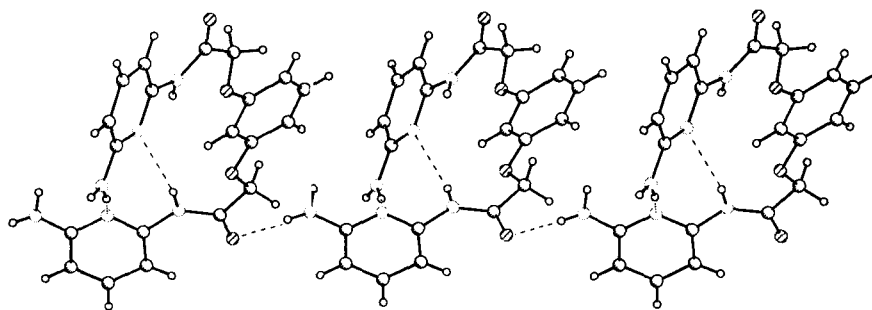


Figure 7. X-ray structure of the packing of **4** (view down the axis b)

In summary, compounds **1** and **2**, which possess an amide NH, a carboxy O atom and pyridine N atom prefer to interact through amide-NH $\cdots$ N-pyr hydrogen bonds. The typical amide-NH $\cdots$ O=C hydrogen bond motif commonly found for secondary diamides is not formed. If the molecule contains amino groups (compounds **3** and **4**) this group is preferred over the amide group as hydrogen bond donor. Compound **3**, with a rigid isophthalic spacer, uses only the amino groups in the hydrogen bond pattern, forming both (H)NH $\cdots$ O=C and (H)NH $\cdots$ N-pyr interactions. The amide NH is not involved. If the flexibility of the molecule also allows short contacts with the amide NH, as in compound **4**, then amide-NH $\cdots$ N-pyr contacts, not amide-NH $\cdots$ O=C hydrogen bonds, are formed. The amide oxygen atoms participate in the formation of NH $\cdots$ O=C hydrogen bonds only if an amino group is part of the molecular structure (compounds **3** and **4**). Additionally, CH $\cdots$ O interactions play an important role in the stabilization of the crystal structures.

## EXPERIMENTAL

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured using a Bruker AMX 300 spectrometer in  $\text{CDCl}_3$  or  $\text{THF-d}_8$  solution, with tetramethylsilane as an internal standard. Mass spectra were obtained with a Fisons VG Prospec 3000 and a Hewlett Packard HP 5971A MSD spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. Thin layer chromatography was carried out on silica gel 60 F $_{254}$  (Merck) thin layer chromatography plates using a methanol/chloroform mixture 1:7 v/v as mobile phase.

*General procedure for the synthesis of 1-4:* To a solution of 2,6-diaminopyridine or 2-amino-6-methylpyridine (0.04 mol) and triethylamine (0.02 mol) in THF (50 ml) was added dropwise a THF solution of isophthaloyl dichloride or *m*-phenylenedioxy-diacyl chloride (0.01 mol) at room temperature. The reaction mixture was stirred for 15 h and then 100 ml water was added. The mixture was stirred for 20 min, then THF was removed under reduced pressure. The precipitate was filtered off and washed several times with water to remove an excess of the aminopyridine derivative and triethylamine hydrochloride. The crude product was crystallized from THF/hexane or benzene/acetic acid ethyl ester.

*1,3-Bis[[6-methyl-pyridin-2-yl]amino]carbonyl]benzene (1)*: M.p. 139-140 °C (benzene / acetic acid ethyl ester 1:3 v/v).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.38 (s, 6H, 2 x  $\text{CH}_3$ ), 6.87-6.91 ( $2\text{H}_{\text{arom}}$ ), 7.59-7.65 ( $3\text{H}_{\text{arom}}$ ), 8.06-8.17 ( $4\text{H}_{\text{arom}}$ ), 8.47-8.49 ( $1\text{H}_{\text{arom}}$ ), 9.05 (s, 2H, 2 x NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.75 ( $\text{CH}_3$ ), 110.77, 119.45, 125.57, 129.24, 130.59, 134.72, 138.61, 150.32, 156.75, 164.21 (CONH). MS m/z (rel. int. %): 346 (85,  $\text{M}^+$ ), 317 (52), 239 (100), 212 (38), 183 (14), 170 (31), 135 (51), 109 (14), 104 (10), 92 (33), 76 (24), 65 (13), 42 (16).  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$ : Calcd. 346.1430 found 346.1422.  $R_f = 0.66$ . Yield 94 %.

*1,3-Bis[[6-methyl-pyridin-2-yl]amino]carbonyl-methoxy]benzene (2)*: M.p. 84.5-85 °C (THF/hexane).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.45 (s, 6H, 2 x  $\text{CH}_3$ ), 4.58 (s, 4H, 2 x  $\text{OCH}_2$ ), 6.63-6.67 ( $3\text{H}_{\text{arom}}$ ), 6.90-6.93 ( $2\text{H}_{\text{arom}}$ ), 7.22-7.28 ( $1\text{H}_{\text{arom}}$ ), 7.57-7.62 ( $2\text{H}_{\text{arom}}$ ), 8.03-8.06 ( $2\text{H}_{\text{arom}}$ ), 8.86 (s, 2H, 2 x NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.80 ( $\text{CH}_3$ ), 68.26 ( $\text{CH}_2$ ), 103.50, 109.15, 11.89, 120.71, 131.50, 139.54, 150.47, 157.86, 159.05, 167.25 (CONH). MS m/z (rel. int. %): 407 (3.6), 406 (1), 271 (65), 243 (8), 165 (8), 149 (100), 136 (18), 121 (18), 108 (34), 92 (22), 81 (3), 65 (9), 39 (5).  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4$ : Calcd. 406.1641 found 406.1629.  $R_f = 0.78$ . Yield 89 %.

*1,3-Bis[[6-amino-pyridin-2-yl]amino]carbonyl]benzene (3)*: M.p. 198 °C (THF/hexane 2:1 v/v; ref.<sup>16</sup> 201-202 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ ):  $\delta$  5.21 (s, 4H, 2 x  $\text{NH}_2$ ), 6.18-6.29 ( $2\text{H}_{\text{arom}}$ ), 7.33-7.39 ( $2\text{H}_{\text{arom}}$ ), 7.55-7.64 ( $3\text{H}_{\text{arom}}$ ), 8.11-8.15 ( $2\text{H}_{\text{arom}}$ ), 8.54-8.55 ( $1\text{H}_{\text{arom}}$ ), 9.51 (s, 2H, 2 x NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{THF-d}_8$ ):  $\delta$  102.91, 104.36, 126.98, 129.31, 131.71, 136.35, 139.67, 151.85, 159.53, 165.33 (CONH). MS m/z (rel. int. %): 348 ( $\text{M}^+$ , 100), 319 (35), 240 (96), 213 (46), 195 (13), 184 (26), 170 (48), 136 (45), 110 (16), 104 (14), 93 (32), 76 (29), 65 (7), 43 (19).  $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_2$ : Calcd. 348.1335 found 348.1368.  $R_f = 0.25$ . Yield 93 %.

*1,3-Bis[[6-amino-pyridin-2-yl]amino]carbonyl-methoxy]benzene (4)*: M.p. 204-205 °C (THF/hexane).  $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ ):  $\delta$  4.48 (4H, s, 2 x  $\text{OCH}_2$ ), 5.17 (s, 4H, 2 x  $\text{NH}_2$ ), 6.03-6.06 ( $2\text{H}_{\text{arom}}$ ), 6.54-6.58 ( $2\text{H}_{\text{arom}}$ ), 6.67 ( $1\text{H}_{\text{arom}}$ ), 7.11-7.23 ( $3\text{H}_{\text{arom}}$ ), 7.31 ( $2\text{H}_{\text{arom}}$ ), 8.56 (s, 1H, NH).  $^{13}\text{C}$  NMR (300 MHz,  $\text{THF-d}_8$ ):  $\delta$  65.79 ( $\text{OCH}_2\text{CO}$ ), 99.36, 100.53, 101.92, 106.16, 128.40, 137.06, 147.96, 157.03, 157.33, 163.83 (CONH). MS m/z (rel. int. %): 408 ( $\text{M}^+$ , 6), 350 (1), 294 (0.5), 272 (100), 244 (21), 205 (6), 166 (9), 151 (19), 149 (27), 136 (63), 122 (38), 109 (99), 93 (46), 82 (17).  $\text{C}_{20}\text{H}_{20}\text{N}_6\text{O}_4$ : Calcd. 408.1500 found 408.1546.  $R_f = 0.30$ . Yield 78 %.

#### X-RAY CRYSTALLOGRAPHIC ANALYSIS

The data of the crystals of **1-4**<sup>22</sup> were obtained with a Siemens SMART-CCD three circle diffractometer ( $\text{MoK}\alpha$ -radiation, graphite-monochromator) at 293 K. The structures were solved using Direct Methods and refined on  $F^2$  using SHELXTL (Vers. 5.03). All non-H atoms were anisotropically refined and aromatic and methyl H atoms were treated as riding groups with the 1.2 fold U-value (1.5 for methyl hydrogens) of the corresponding C-atoms. The mentioned distances to H-atoms are based on normalized C-H distances ( $d_{\text{C-H}} = 1.08 \text{ \AA}$ ).

*Crystal data for 1:* C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> · 0.5 H<sub>2</sub>O, M = 355.14, crystal dimensions 0.32 x 0.21 x 0.06 Å<sup>3</sup>, crystal system monoclinic, space group C2c, a = 26.7228(4), b = 7.7454(1), c = 21.9357(4) Å, α = 90, β = 126.269, γ = 90°, V = 3660.55(9) Å<sup>3</sup>, Z = 8, ρ<sub>calcd</sub> = 1.289 gcm<sup>-3</sup>, wavelength 0.71073 Å, 19790 reflections collected (full sphere, θ-range 1.89–28.25°), 4502 independent reflections (R<sub>int</sub> = 0.0555, empirical absorption correction), 2373 observed [F<sub>o</sub> ≥ 4σ(F<sub>o</sub>)], 250 parameters, R1 = 0.0545, wR2 = 0.1356, residual electron density 0.294 eÅ<sup>-3</sup>, μ = 0.088 mm<sup>-1</sup>, max/min transmission 1.00 / 0.75.

*Crystal data for 2:* C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>, M = 406.44, crystal dimensions 0.43 x 0.32 x 0.25 Å<sup>3</sup>, crystal system monoclinic, space group P2<sub>1</sub>c, a = 8.625(3), b = 26.530(8), c = 9.459(2) Å, α = 90, β = 105.19(2), γ = 90°, V = 2088.8(10) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.292 gcm<sup>-3</sup>, wavelength 0.71073 Å, 2984 reflections collected (full sphere, θ-range 1.54–22.66°), 2778 independent reflections (R<sub>int</sub> = 0.0572, empirical absorption correction), 1267 observed [F<sub>o</sub> ≥ 4σ(F<sub>o</sub>)], 271 parameters, R1 = 0.0747, wR2 = 0.1907, residual electron density 0.177 eÅ<sup>-3</sup>, μ = 0.091 mm<sup>-1</sup>, max/min transmission 1.00 / 0.71.

*Crystal data for 3:* C<sub>18</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub> · H<sub>2</sub>O, M = 366.38, 298 K, crystal dimensions 0.28 x 0.25 x 0.13 Å<sup>3</sup>, crystal system orthorhombic, space group Pccn, a = 12.2508(2), b = 12.6796(4), c = 22.5379(8) Å, α = β = γ = 90°, V = 3500.9(2) Å<sup>3</sup>, Z = 8, ρ<sub>calcd</sub> = 1.390 gcm<sup>-3</sup>, wavelength 0.71073 Å, 31333 reflections collected (full sphere, θ-range 2.31–24.73°), 2996 independent reflections (R<sub>int</sub> = 0.0927, empirical absorption correction), 1915 observed [F<sub>o</sub> ≥ 4σ(F<sub>o</sub>)], 244 parameters, R1 = 0.0748, wR2 = 0.1340, residual electron density 0.213 eÅ<sup>-3</sup>, μ = 0.099 mm<sup>-1</sup>, max/min transmission 1.00 / 0.76.

*Crystal data for 4:* C<sub>20</sub>H<sub>20</sub>N<sub>6</sub>O<sub>4</sub>, M = 408.42, crystal dimensions 0.26 x 0.19 x 0.12 Å<sup>3</sup>, crystal system monoclinic, space group P2<sub>1</sub>c, a = 18.5455(5), b = 6.5811(2), c = 17.4905(5) Å, α = 90, β = 111.3920, γ = 90°, V = 1987.64(10) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.365 gcm<sup>-3</sup>, wavelength 0.71073 Å, 22707 reflections collected (full sphere, θ-range 2.34–28.26°), 4914 independent reflections (R<sub>int</sub> = 0.0304, empirical absorption correction), 3045 observed [F<sub>o</sub> ≥ 4σ(F<sub>o</sub>)], 284 parameters, R1 = 0.0578, wR2 = 0.1325, residual electron density 0.245 eÅ<sup>-3</sup>, μ = 0.099 mm<sup>-1</sup>, max/min transmission 1.00 / 0.94.

**Acknowledgments:** A *Lise-Meitner* stipend of the *Fonds zur Förderung des Wissenschaftlichen Nachwuchses* to M. M. is gratefully acknowledged. We thank the *Deutsche Forschungsgemeinschaft* for financial support (SFB 452).

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22. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127786 (1), 127787 (2), 127785 (3) and 127784 (4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).