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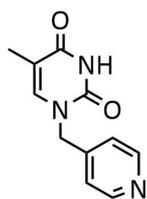
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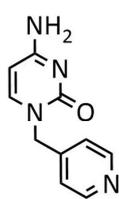
Molecular tectonics: self-assembly of pyridyl bearing nucleobases

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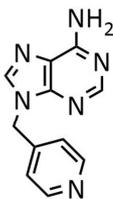
Elsa Tufenkjian, Abdelaziz Jouaiti, Nathalie Kyritsakas, Mir Wais Hosseini, Veronique Bulach
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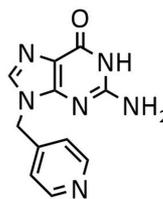
T-Py



C-Py



A-Py



G-Py



Molecular tectonics: self-assembly of pyridyl bearing nucleobases

Elsa Tufenkjian, Abdelaziz Jouaiti, Nathalie Kyritsakas, Mir Wais Hosseini*, and Veronique Bulach*

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ABSTRACT

A library of organic tectons (**1-3** and **5**) combining nucleobases and a pyridyl moiety connected at the position 4 of the ring was designed and synthesized. The solid-state structure of tectons **1-3** was investigated by X-ray diffraction on single crystal. Owing to the self-complementary nature of the tectons bearing both H-bond donor and acceptor sites, compounds **1-3** self-assemble into H-bonded networks. The dimension of the latter is further increased when taking into account π - π stacking interactions.

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1. Introduction

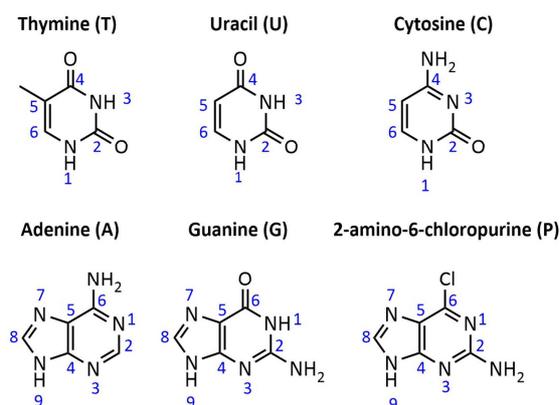
The design of periodic architectures in the crystalline phase is the main subject of molecular tectonics.¹ The formation of these supramolecular assemblies² described as molecular networks³ is based on the design of complementary or self-complementary tectons. The generation of extended architectures in the solid-state results from the self-assembly of molecular components composing the crystal. A common strategy to generate molecular networks relies on the use of iterative molecular recognition processes between tectons based on a variety of intermolecular interactions. In particular, hydrogen bonding has been widely explored.⁴ The latter, taking place between H-bond donor and acceptor sites, is rather directional and thus of interest for the generation of hydrogen bonded polymers or molecular networks.⁵

Nucleobases (NBs) such as thymine (T), uracil (U), cytosine (C), adenine (A) and guanine (G), present in DNA and RNA, are ubiquitous in biology. These molecules are simultaneously H-bond donors and acceptors and therefore may be regarded as complementary and self-complementary tectons (Scheme 1). In particular complementary NB pairs such as A and T or G and C form Watson-Crick type H-bonds.⁶ In addition to these recognition patterns, approximately 30 other possible H-bond interactions may occur by combining the above-mentioned NBs.⁷

Functionalized NBs and their combinations have been explored for the formation of molecular networks based on NBs.⁸ Similarly, we envisioned designing H-bonded networks based on nucleobases functionalized by a pyridine. We report here the design, synthesis and characterization of four pyridyl bearing tectons **1-3** and **5** based on four different nucleobases. Moreover,

we also describe the formation of H-bonded molecular networks in the crystalline phase for tectons **1-3**.

The presence of a pyridyl unit open new possibilities such as formation of hybrid networks combining H- and coordination-bonds in the presence of metal cations. Such networks have also been investigated and will be reported elsewhere.



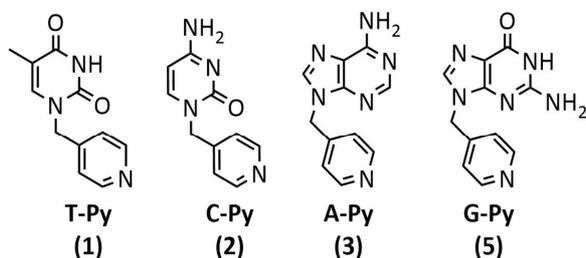
Scheme 1. Nucleobases (NBs) and derivatives

2. Results and Discussion

2.1. Design and synthesis

The nucleobases A, T, C and G are self-complementary H-bond donor and acceptor units (Scheme 1). The design of tectons

1-3 and **5** is based on the functionalization of the above-mentioned nucleobases by a pyridyl unit as a peripheral H-bond acceptor moiety (Scheme 2). The position 4 on the pyridyl is used to connect the latter to the nucleobases (Scheme 2), resulting into tectons having two divergent H-bonding sites *via* a flexible linker. For both Thymine (T) and Cytosine (C), the pyridyl unit is connected to the position N1 whereas for Adenine (A) and Guanine (G), it is attached at position N9 (Scheme 2).



Scheme 2. Molecular structure of the targeted tectons

The synthesis of tectons **1-3** and **5** was achieved by substitution reaction between a chosen nucleobase and 4-(bromomethyl)pyridine (Scheme 3). The conditions of the reactions were modified following known procedures to result the best yield of the targeted tectons.^{9,10}

The products were characterized by NMR and infrared spectroscopies as well as by high-resolution mass spectrometry and crystallography on single crystal.

Thymine-pyridine, tecton **1**, was obtained by reacting 3 equivalents of thymine (T) and 1 equivalent of 4-(bromomethyl)pyridine hydrobromide in the presence of 2.5 equivalents of K_2CO_3 and a catalytic amount of KI in dry DMF. The base was added in excess to neutralize the hydrobromide salt and to deprotonate the nucleobase. Thymine may be substituted at both positions N1 and N3.¹⁰ To decrease the yield of the disubstituted derivative, thymine was used in excess. The unreacted thymine and K_2CO_3 were removed by washing with water. The disubstituted and monosubstituted products were separated by column chromatography leading to **1** in 45% yield.

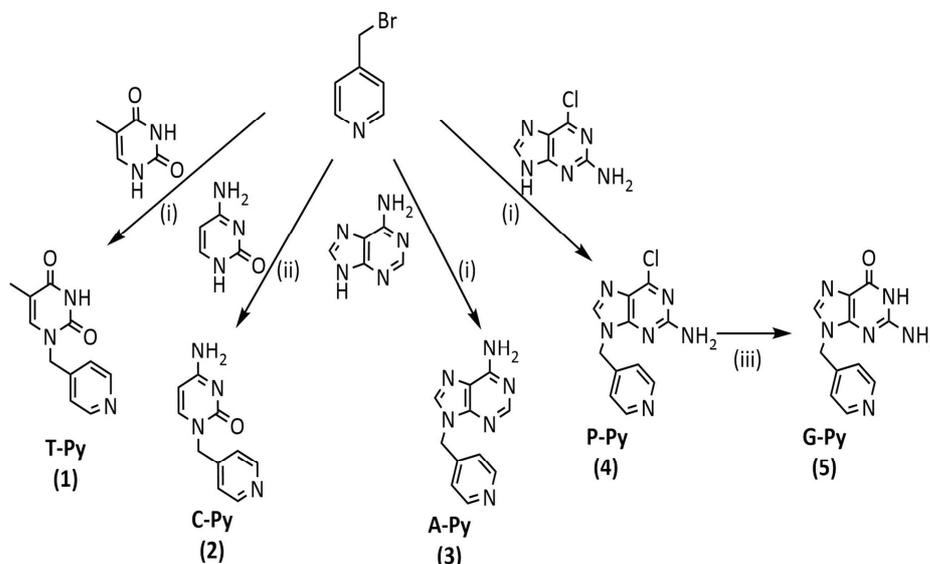
In the case of cytosine (C), the use of K_2CO_3 gave a very low yield. Deprotonation of cytosine at position N1 was achieved using tBu_4NOH ¹⁰ or NaH ¹¹. The best condition for the preparation of cytosine-pyridine, tecton **2**, was to react an excess of cytosine (3 equivalents) and 1 equivalent of 4-(bromomethyl)pyridine hydrobromide in the presence of 2.5 equivalents of NaH and a catalytic amount of KI in dry DMF. This procedure afforded the desired compound **2** in 30% yield. ¹H-NMR analysis showed the presence of the pyridyl at position N1, since the signal of NH1 proton disappeared and two broad singlets for NH2 protons appear at 7.08 and 7.21 ppm in agreement with the tautomeric form of cytosine.^{10,11}

The synthesis of adenine-pyridine, tecton **3**, was achieved following the same conditions as for **1**. Two equivalents of adenine was reacted with 1 equivalent of 4-(bromomethyl)pyridine hydrobromide in the presence of 2.5 equivalent of K_2CO_3 and catalytic amount of KI in dry DMF leading to the functionalization of adenine at position N9. Compound **3** was obtained in 53% yield.

To synthesize the guanine-pyridine, tecton **5**, the direct reaction of guanine with 4-(bromomethyl)pyridine hydrobromide was first performed. However, it afforded an insoluble product that was difficult to purify. Thus, 2-amino-6-chloropurine (Scheme 1), a more soluble purine easily hydrolysable to guanine^{11,12} was used. Therefore, the synthesis of the last targeted tecton **5** was achieved in two steps (scheme 3). First, reacting 2 equivalents of 2-amino-6-chloropurine with 1 equivalent of 4-(bromomethyl)pyridine hydrobromide in the presence of 2.5 equivalents of K_2CO_3 and a catalytic amount of KI in dry DMF yielded 2-amino-6-chloropurine-pyridine, tecton **4**, in 30% yield. The latter was hydrolysed using 0.1 M HCl aqueous solution leading to compound **5** in 96% yield.

2.2. Solid State Structures of the Tectons

Single crystals of tectons **1-3** were grown by slow evaporation of a mixture of dichloromethane and cyclohexane (1:1) containing the tecton and characterized by X-ray crystallography on single crystal (Figure 1). For the tecton **4** and **5**, different conditions and methods were used to grow single crystals, unfortunately without success.



Scheme 3. General procedure for the synthesis of compounds (**1-5**). (i) K_2CO_3 , KI, DMF, 40 °C, 12 h (ii) NaH , KI, 40 °C, 12 h (iii) 0.1 M HCl (aq), reflux, 5 h

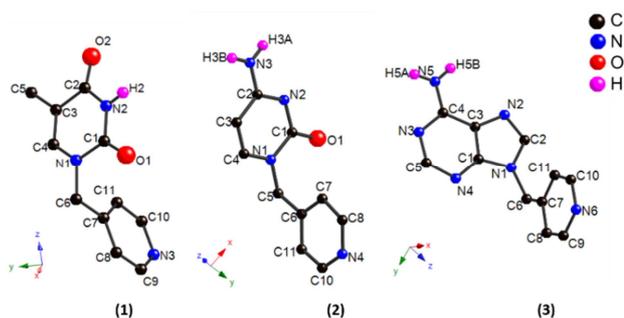


Figure 1. Crystal Structures of tectons 1-3. H atoms except those shown were omitted for clarity.

2.2.1. Crystal Structure of T-Py (1)

Thymine-pyridine crystallizes in Monoclinic space group $P 2_1/n$. The pyridyl unit is almost perpendicular to the thymine mean plane with an angle of 89° . The tecton self-assembles through H-bonds between the N atom of the pyridyl moiety and the thymine NH group with a d_{N2-N3} distance of 2.85 \AA leading consequently to a 1D zig-zag type chain. Consecutive zig-zag chains are stacked in an antiparallel fashion. When considering the π - π interactions (centroid separation of 3.50 \AA), the overall architecture may be described as superposition of 2D networks generated through both H-bonding and π - π stacking (Figure 2).

It is interesting to notice that the 1D H-bonded chain does not involve H-bonds between two thymine moieties, but results from the establishment of a H-bond between a Py and a T moiety. Within 1D-chain, the distance observed between pyridine and thymine moieties is close to 1.99 \AA (d_{N3-H2}), while an average $H \cdots O$ distance of 2.25 \AA is usually observed between two H-bonded thymine.^{6(b), 13} The zig-zag pattern of the H-bonded chain is possible because of the flexibility of the CH_2 linker between the pyridyl moiety and the thymine and the π - π interactions between adjacent chains explaining the packing of the chains. These observations prove that by controlling the nature and structure of the peripheral H-bonding sites different assemblies can occur based on the flexibility of the molecules, competition between the H-bonds and secondary interactions that favor one assembly over the other.

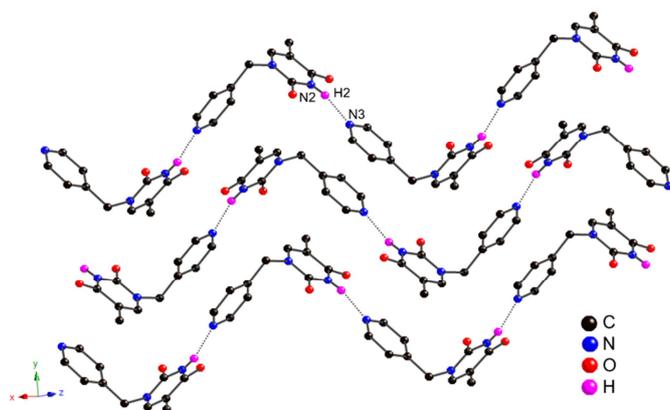


Figure 2. A portion of the crystal Structure of 1 showing the formation of a 1D H-bonded network and the packing of consecutive zig-zag chains by π - π stacking leading to a 2D architecture. For bond distances and angles see text.

2.2.2. Crystal Structure of C-Py (2)

Cytosine-pyridine crystallizes in Monoclinic space group $P 2_1/c$. Again, the pyridyl unit is almost perpendicular to the cytosine mean plane with an angle of $ca 85^\circ$. Consecutive tectons interconnect by hydrogen bonds between the cytosine moieties leading to a 1D network (Figure 3a). The cytosine moieties act as two H-bond donors (through their NH_2 sites) and as two H-bond acceptors (through the O1 and N2 atoms). Thus, each tecton is in interaction with three adjacent tectons, *via* the cytosine rings, through four different H-bonds with distances d_{N3-O1} of 2.89 \AA , and d_{N3-N2} of 3.01 \AA . In this structure the H-bonding interactions are more favored than the interaction between the cytosine and the pyridyl moiety, since the pyridines are not involved in the H-bonding interactions. Consecutive chains are stacked *via* π - π interactions between the cytosine rings, which are located above each other with a centroid-centroid separation of 3.48 \AA . Figure 3 (b) shows a side view of the chain and its translation in space.

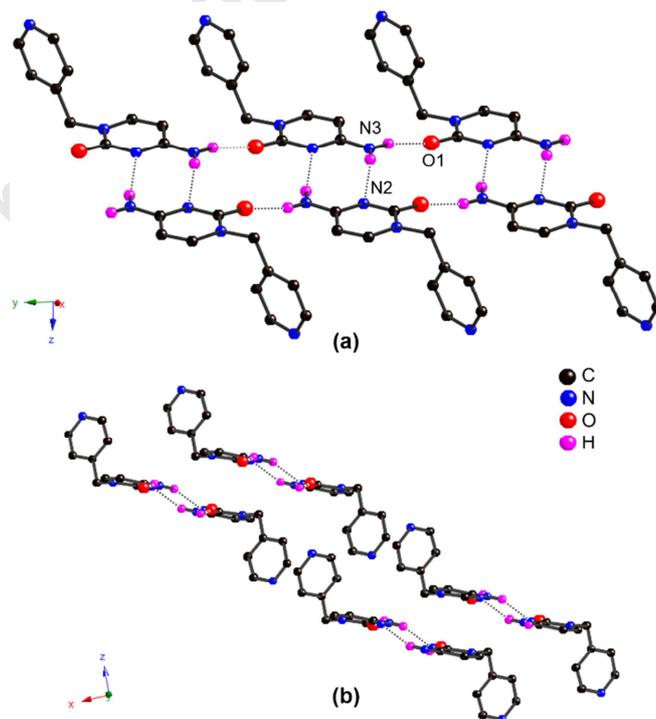
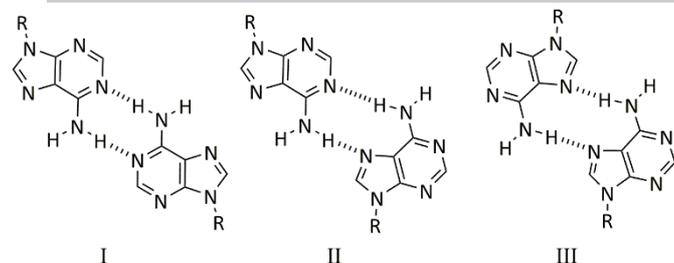


Figure 3. Portions of crystal Structure of 2 showing (a) the H-bonding pattern leading to a 1D chain, (b) π - π stacking between two consecutive chains.

2.2.3. Crystal Structure of A-Py (3)

Adenine-pyridine crystallizes in Monoclinic space group $P 2_1/c$. The angle between the pyridyl and the adenine mean plane is close to 76° . Two tectons 3 form an H-bonded dimer *via* two hydrogen bonds between the adenine moieties with a d_{N3-N5} distance of 3.01 \AA . These interactions demonstrate the Watson-Crick H-bonding interactions between two adenine molecules. The dimeric arrangement of tectons 3 is one of three most common dimeric arrangements of functionalized adenines (Scheme 4).⁸⁽ⁱ⁾ According to reported calculations, the order of the stabilization energy of the three dimeric arrangements is: I



(Watson-Crick interaction) > II > III (Hoogsteen interaction), which clarifies the formation of the dimeric assembly of tectons **3**.¹⁴

Scheme 4. The H-bonded dimeric arrangements of functionalized adenine

Moreover, the self-assembly of **3** is supported by additional π -

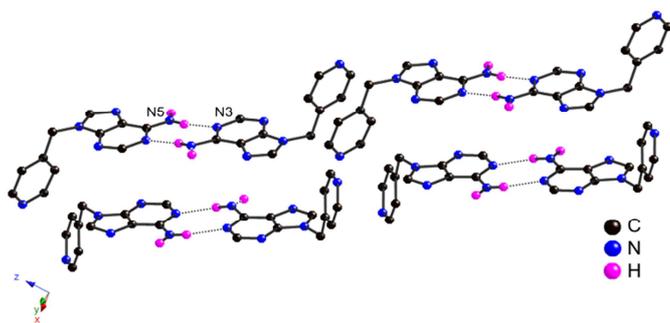


Figure 4. A portion of the crystal Structure of **3** showing the H-bonding pattern and packing through π - π stacking between consecutive tectons

π interactions between dimers. Adenines of adjacent dimers are involved in π - π interaction with a centroid-centroid separation of 3.5 Å. Moreover, each pyridyl moiety interacts with another pyridyl unit of an adjacent dimer with a distance between the centroids of ca 3.6 Å (Figure 4).

3. Conclusions

In summary, the synthesis of four new organic tectons **1-3** and **5** based on four nucleobases T, A, C and G bearing a pyridyl H-bond acceptor moiety was achieved. Three out of the four tectons (**1-3**) have been characterized in the solid state by X-ray diffraction on single crystals. Owing to the self-complementary nature of tectons, *i.e.* presence of both H-bond donor and acceptor sites, all three tectons **1-3** lead to the formation of H-bonded molecular networks. Whereas for both tectons **2** and **3** the expected H-bond pattern was observed, for the tecton **1** another type of connectivity involving the pyridyl unit as a H-bond acceptor was observed. Interestingly, when taking into account π - π interactions, in all three cases, the overall architecture may be described as 2D networks.

We also studied the formation of H-bonded networks based on complementary pairs such as T-Py /A-Py or C-Py/G-Py. Unfortunately, despite many attempts, no single crystals could be isolated.

However, the presence of a pyridyl unit open other possibilities such as formation of hybrid networks combining H- and coordination-bonds in the presence of metal cations. Such

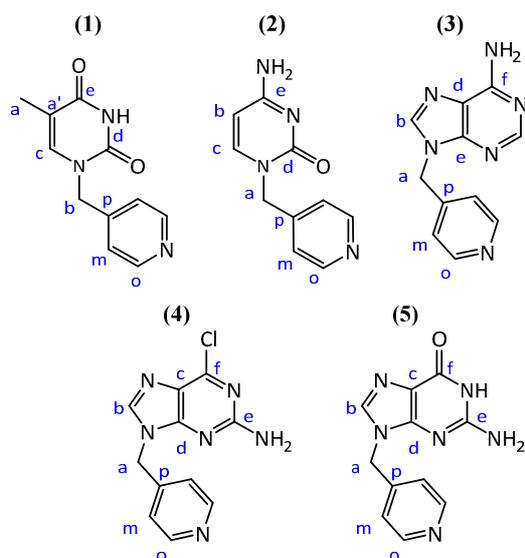
Pre-networks have been obtained and their structural characterization by X-Ray diffraction will be reported shortly.

4. Experimental section

The starting materials were purchased from commercial suppliers and used without further purification. All reactions were performed under argon and followed by TLC. Column Chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 Å). NMR spectra were recorded on a Bruker AC or AV-300, AV-400 or AV-500 at room temperature. The chemical shifts are reported in ppm using the signal of CDCl₃ calibrated at 7.26 ppm (¹H-NMR) and 77.16 ppm (¹³C-NMR) or d₆-DMSO calibrated at 2.50 ppm (¹H-NMR) and 39.50 ppm (¹³C-NMR) as internal standards. High-resolution mass spectra (HRMS) were recorded on an Applied Biosystem QSTAR instrument (ESI). IR spectra were recorded on a Perkin-Elmer Spectrum Two FT-IR spectrometer.

4.1. General procedure (A)

The nucleobase, K₂CO₃ and catalytic amounts of KI were mixed in dry DMF. The suspension was degassed with argon for 15 minutes. A solution of 4-(bromomethyl)pyridine hydrobromide in dry DMF was added slowly to the suspension. The mixture was stirred under argon at 40 °C overnight and the reaction progress was followed by TLC. The crude was dried under vacuum and purified by column chromatography (silica gel, MeOH: Et₃N: DCM 1:0.2:20).



Scheme 5. Compounds **1-5** with labelling for NMR assignment.

4.2. Thymine-pyridine (**1**)

Thymine-pyridine (**1**) was obtained following the general procedure **A** using thymine (0.75 g, 5.94 mmol, 3 eq), 4-(bromomethyl)pyridine (0.5 g, 1.98 mmol, 1 eq), K₂CO₃ (0.68 g, 4.95 mmol, 2.5 eq), KI (10 mg, catalytic amount) and DMF (17 mL + 4 mL). The crude was purified by column chromatography to yield compound **1** (190 mg, 45%) as a white solid; d_H (500 MHz, CDCl₃) 1.92 (3H, d, ⁴J = 1.1 Hz, Ha), 4.90 (2H, s, Hb), 6.96 (2H, q, ⁴J = 1.1 Hz, Hc), 7.19 (2H, d, ³J = 6.0 Hz, Hm), 8.62 (2H, d, ³J = 6.0 Hz, Ho); d_C (126 MHz, CDCl₃) 12.74 (Ca), 50.4 (Cb), 112.3 (Ca'), 122.5 (Cm), 144.7 (Cc), 150.9 (Cp), 151.2 (Co), 151.2 (Cd), 164.0 (Ce); HRMS (ESI): MH⁺, found 218.0926. C₁₁H₁₁N₃O₂ requires 218.0924; IR ν (cm⁻¹): 2996.47,

2927.84, 2748.17, 2680.68, 1600.60, 1444.94, 14717.47, 1382.30, 1345.79, 1314.90, 1226.61, 1214.96, 1065.16, 1006.63, 912.75, 799.56, 764.92, 540.07, 483.43, 465.95, 408.37.

4.3. Cytosine-pyridine (2)

Cytosine-pyridine (**2**) was obtained by mixing cytosine (0.65 g, 5.93 mmol, 3 eq) and KI (10 mg, catalytic amount) in 10 mL of dry DMF. After degassing the suspension with argon for 15 minutes, NaH (0.118 g, 4.9 mmol, 2.5 eq) was added and the mixture was stirred for 30 minutes. A solution of 4-(bromomethyl)pyridine hydrobromide (0.5 g, 1.97 mmol, 1 eq) in 4 mL of dry DMF was slowly added to the mixture. The mixture was stirred at 40 °C overnight and the reaction progress was followed by TLC. The crude was dried under vacuum and then washed with a minimum amount of water. The product was purified by column chromatography (silica gel, MeOH: Et₃N: DCM 1:0.2:20) affording compound **2** (120 mg, 30%) as a white powder; d_H (500 MHz, DMSO-*d*₆) 4.87 (2H, s, Ha), 5.73 (1H, d, ³*J* = 7.2 Hz, Hb), 7.08 (1H, s, brd, NH), 7.17 (2H, d, ³*J* = 6.0 Hz, Hm), 7.21 (1H, s, brd, NH), 7.69 (1H, d, ³*J* = 7.2 Hz, Hc), 8.50 (2H, d, ³*J* = 6.0 Hz, Ho); d_C (126 MHz, DMSO-*d*₆) 50.6 (Ca), 93.9 (Cb), 122.0 (Cm), 146.1 (Cc), 147.0 (Cp), 149.7 (Co), 155.7 (Cd), 166.1 (Ce); HRMS (ESI): MH⁺, found 203.0934. C₁₀H₁₀N₄O requires 203.0927; IR ν (cm⁻¹): 3337.24, 3115.39, 1652.03, 1597.71, 1486.09, 1423.17, 1384.39, 1369.72, 1278.91, 1208.06, 1130.29, 965.29, 815.97, 781.56, 704.43, 682.80, 567.57, 521.43, 474.65, 405.44.

4.4. Adenine-pyridine (3)

Adenine-pyridine (**3**) was obtained following the general procedure **A** presented above using adenine (0.39 mg, 2.92 mmol, 2 eq), K₂CO₃ (0.51 g, 3.7 mmol, 2.5 eq), KI (10 mg, catalytic amount), 4-(bromomethyl)pyridine hydrobromide (0.37 g, 1.46 mmol, 1 eq) and dry DMF (10 mL + 4 mL). The product was purified by column chromatography and afforded compound **3** (177 mg, 53%) as a white solid; d_H (500 MHz, DMSO-*d*₆) 5.43 (2H, s, Ha), 7.18 (2H, d, ³*J* = 6.0 Hz, Hm), 7.30 (2H, s, brd, NH₂), 8.12 (1H, s, Hb), 8.28 (1H, s, Hc), 8.51 (2H, d, ³*J* = 6.0 Hz, Ho); d_C (126 MHz, DMSO-*d*₆) 45.1 (Ca), 118.7 (Cd), 122.0 (Cm), 141.0 (Cb), 145.9 (Ce), 149.5 (Cp), 145.0 (Co), 152.8 (Cc), 156.1 (Cf); HRMS (ESI): MH⁺, found 227.1025. C₁₁H₁₀N₆ requires 227.1040; IR ν (cm⁻¹): 3309.03, 3086.81, 1647.03, 1571.57, 1596.00, 1484.87, 1415.54, 1389.08, 1356.11, 1326.47, 1246.47, 1155.32, 1069.89, 1006.32, 970.50, 877.84, 796.02, 772.66, 726.04, 649.69, 852.69, 542.45, 464.88.

4.5. 2-amino-6-chloropurine-pyridine (4)

2-amino-6-chloropurine-pyridine (**4**) was obtained following general procedure **A** using 2-amino-6-chloropurine (0.8 g, 4.74 mmol, 2 eq), K₂CO₃ (0.81 g, 5.9 mmol, 2.5 eq), KI (10 mg, catalytic amount) and 4-(bromomethyl)pyridine hydrobromide (0.6 g, 2.37 mmol, 1 eq) and dry DMF (10 mL + 4 mL). The product was purified by column chromatography (silica gel, MeOH: Et₃N: DCM 1:0.2:20) affording compound (**4**) (185 mg, 30%) as a white solid; d_H (400 MHz, DMSO-*d*₆) 5.36 (2H, s, Ha), 6.92 (2H, s, brd, NH₂Cl-purine), 7.18 (2H, d, ³*J* = 5.9 Hz, Hm), 8.24 (1H, s, Hb), 8.51 (2H, d, ³*J* = 6.0 Hz, Ho); d_C (126 MHz, CDCl₃) 46.0 (Ca), 121.9 (Cm), 125.1 (Cd), 141.9 (Ce), 144.2 (Cp), 150.6 (Co), 151.9 (Cc), 153.9 (Ce), 159.5 (Cf); MS (ESI): MH⁺, found: 261.07. C₁₁H₉N₆Cl requires 261.06; IR ν (cm⁻¹): 3314.94, 3196.50, 2920.71, 1613.77, 1563.79, 1524.55, 1408.74, 1282.37, 1176.00, 1024.20, 999.61, 913.61, 761.91, 720.10.

4.6. Guanine-pyridine (5)

Guanine-pyridine (**5**) was obtained by dissolving the compound **4** (100 mg, 0.384 mmol, 1 eq) in 20 mL of 0.1 M HCl aqueous solution. The mixture was stirred under reflux and its evolution was followed by TLC. The mixture was left to stir for 5 hours until all compound **4** was oxidized into guanine. Then, 0.1 M NaOH solution was added dropwise to neutralize the solution (*ca.* 5 mL) affording a white precipitate, which was filtered and washed with water (10 mL) and acetone (10 mL). The precipitate was dried under reduced pressure to give compound **5** (89 mg, 96%) as a white solid; d_H (500 MHz, DMSO-*d*₆) 5.24 (2H, s, Ha), 6.74 (2H, s, brd, NH₂ guanine), 7.11 (2H, d, ³*J* = 5.6 Hz, Hm), 7.79 (1H, s, Hb), 8.51 (2H, d, ³*J* = 5.6 Hz, Ho), 10.94 (1H, s, brd, NH guanine); d_C (126 MHz, DMSO-*d*₆) 44.8 (Ca), 116.6 (Cc), 121.7 (Cm), 137.5 (Cb), 146.2 (Cp), 149.9 (Co), 151.3 (Cd), 154.2 (Ce), 157.0 (Cf); HRMS (ESI): MH⁺, found: 243.099. C₁₁H₁₀N₆O requires 243.0989; IR ν (cm⁻¹): 3314.45, 1672.96, 1552.12, 1478.50, 1416.53, 1389.63, 1260.55, 1214.50, 1100.85, 775.91, 536.1.

5. X-ray diffraction

Single crystals of the tectons **1-3** were obtained by slow evaporation of a (1:1) mixture of dichloromethane and cyclohexane.

Single X-ray Crystal data were collected on a Bruker Smart CCD diffractometer with Mo-K α radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.¹⁵ The hydrogen atoms were introduced at calculated positions and not refined (riding model). CCDC 1895363, 1895366, 1895362 contain the supplementary crystallographic data for **1**, **2** and **3** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

5.1. Thymine-pyridine (1)

CCDC 1895363, C₁₁H₁₁N₃O₂, M = 217.23, monoclinic, space group P2₁/n, a = 9.9558(4) Å, b = 10.0713(4) Å, c = 10.4627(4) Å, α = 90°, β = 98.785(2)°, γ = 90°, V = 1036.77(7) Å³, Z = 4, μ = 0.099 mm⁻¹, Refls. coll.: 13876, Ind. refls. = 2959 [R(int) = 0.0326], GooF = 1.038, R₁ = 0.0451, wR₂ = 0.1332 for I > 2 σ (I), and R₁ = 0.0563, wR₂ = 0.1414 for all data

5.2. Cytosine-pyridine (2)

CCDC 1895366, C₁₀H₁₀N₄O, M = 202.22, monoclinic, space group P2₁/c, a = 5.8564(12) Å, b = 7.2098(18) Å, c = 22.312(6) Å, α = 90°, β = 95.830(5)°, γ = 90°, V = 937.2(4) Å³, Z = 4, μ = 0.099 mm⁻¹, Refls. coll.: 6451, Ind. refls. = 2251 [R(int) = 0.0897], GooF = 1.085, R₁ = 0.0642, wR₂ = 0.1691 for I > 2 σ (I), and R₁ = 0.0811, wR₂ = 0.1816 for all data

5.3. Adenine-pyridine (3)

CCDC 1895362, C₁₁H₁₀N₆, M = 226.25, monoclinic, space group P2₁/c, a = 11.6706(8) Å, b = 12.2719(13) Å, c = 7.1051(6) Å, α = 90°, β = 90.170(6)°, γ = 90°, V = 1017.59(15) Å³, Z = 4, μ = 0.098 mm⁻¹, Refls. coll.: 17584, Ind. refls. = 2741 [R(int) = 0.0319], GooF = 1.049, R₁ = 0.04372, wR₂ = 0.1065 for I > 2 σ (I), and R₁ = 0.0571, wR₂ = 0.1149 for all data

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: