Exploring the 2,2′-Diamino-5,5′-bipyrimidine Hydrogen-Bonding Motif: A Modular Approach to Alkoxy-Functionalized Hydrogen-Bonded Networks

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The programmed self-association of 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines allows for the *de novo* construction of alkoxy-functionalized H-bonded ribbons and sheets as evidenced by X-ray crystallographic analysis. The data provide insight into the interplay of the different structural and interactional features of the molecular components to the generation of the supramolecular assembly. Hydrophobicity of the didodecyl side chains of **4c** leads to the dominance of the H-bonding factor, resulting in the formation of a fully interconnected array. These results define the utility of the of 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines as a potential scaffold for the attachment of electro- or photochemically active alkoxy residues for self-assembled functional supramolecular materials.

1. Introduction. – As liquid crystallinity, nonlinear optical properties, ferromagnetic behavior, electrical properties, and solid-state reactivity all depend crucially on the relative orientation of the composite molecules in the solid state, much attention has recently been focused on the development of procedures for the *de novo* design of molecular solids, particularly in H-bonded systems [1]. Toward this end, the use of persistent H-bonding motifs as scaffolds for the modular attachment of 'functional' residues represents a particularly promising strategy [2]. In this approach, two elements are combined, a programmed structural component, *i.e.*, the portion of the molecule that encodes for the H-bonding motif, and a functional component which imparts a given physical property. The viability of such a strategy requires a H-bonding motif of sufficient strength for the integrity of structural information that it encodes to be maintained upon introduction of functional residues imparting various physical properties. A key aspect of this approach is the capacity for modular attachment of such functional residues allowing the material properties to be tuned. As part of our general investigation involving self-assembly in H-bonded systems[1]), we here report

[1]) For homo- and heteroleptic components for the formation of molecular ribbons, see [3a]; for molecules that specifically recognize mismatched base pairs in DNA strands, see [3b]; for polymeric liquid crystalline supramolecular materials, see [3c]; for recognition units for the specific aggregation and fusion of vesicles, see [3d]; for templates for deconvolution/selection in dynamic combinatorial libraries, see [3e].

initial studies toward modularly functionalized H-bonded networks that explore the behavior of the structural motif expressed by the 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines as a function of the 4,4′-dialkoxy substitution introduced.

2. Design Strategy. – Our present design of a molecular component encoding specific structural information takes advantage of the known homomeric H-bonding motif expressed by 2-aminopyrimidines. In the solid state, 2-aminopyrimidines assemble to form H-bonded ribbons [4]. Combining such one-dimensional motifs *via* covalent connection of two 2-aminopyrimidines at the 5,5′-positions should allow for propagation in a second dimension thus yielding a surface. The capacity for modular introduction of a given functional component is realized in the ability of 4-halopyrimidines to undergo alkoxy substitution. It was thus of interest to investigate how, in the alkoxy-functionalized bipyrimidine **1**, this substituent would influence the expression of the H-bonding features. Steric approach to one face of the 2-aminopyrimidine may be impeded so as to yield ribbons of dimers, as depicted schematically in **A**, in which the alkoxy substituents of each bipyrimidine are arranged in a *trans*-fashion, or **B**, where the alkoxy substituents of each bipyrimidine are arranged in a *cis*-fashion. Alternatively, the surface may persist unperturbed as in **C** (*Fig. 1*).

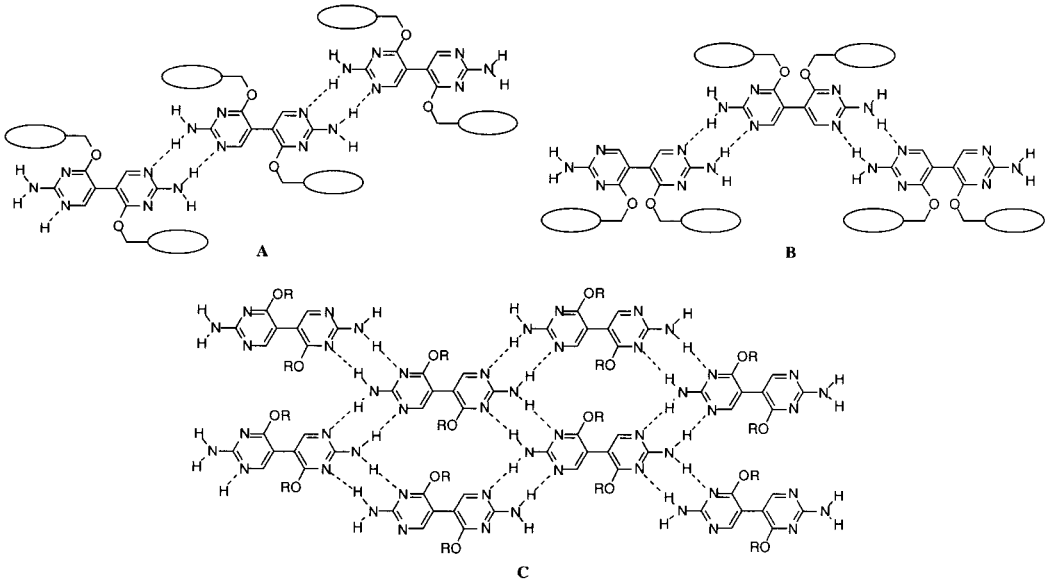
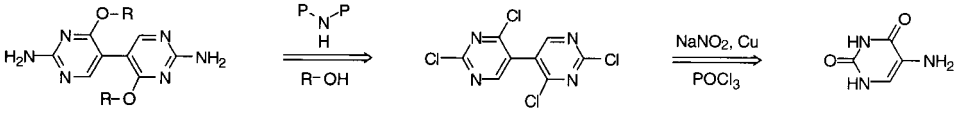


Fig. 1. *Possible one- and two-dimensional H-bonded networks that may be generated from 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines*

3. Synthesis of the Molecular Components. – For the synthesis of the molecular components, it was desirable to develop a convergent, modular sequence that would lend itself to the preparation of a series of analogous compounds in large quantities. The retrosynthetic analysis of the 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines **4**

involves amino and alkoxy substitution of the 2,2′,4,4′-tetrachlorobipyrimidine (**1**) which may, in turn, be derived *via* Cu-mediated reductive coupling of 5-diazouracil. The success of this strategy hinged upon the ability to achieve high levels of chemoselectivity in the substitution of **1** (*Scheme 1*).

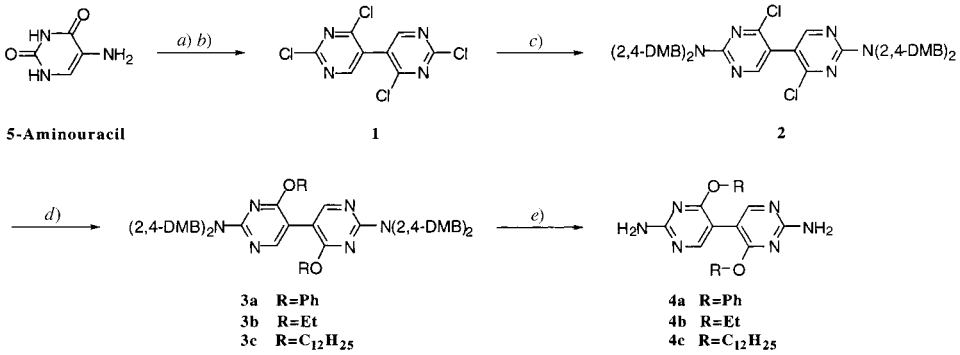
Scheme 1. *Retrosynthetic Analysis of 5,5′-Bipyrimidines* **4**



4 **1** **5-Aminouracil**

Treatment of commercially available 5-aminouracil with $NaNO_2$ under acidic conditions gave the diazo derivative which dimerized upon exposure to Cu powder [5]. The resultant 5,5′-biuracil was converted to the tetrachlorobipyrimidine **1** *via* the literature procedure [6]. Dimethylaminolysis of 2,4-dichloro-5-methylpyrimidine in aqueous Me_2NH is reported to favor substitution exclusively at C(4) [7]. To overcome this strong electronic bias, we reasoned that the use of a sufficiently bulky secondary amine would sterically direct the chemoselectivity of the amine-substitution reaction for the related compound **1** to favor condensation at C(2). Indeed, reaction of **1** with bis(2,4-dimethoxybenzyl)amine [8] gave exclusively the 2,2′-disubstituted bipyrimidine **2** in quantitative yield. Alkoxy substitution of the remaining Cl functionality followed by oxidative removal of the *N*-protecting groups then gave the desired tectons **4a**–**c** (*Scheme 2*).

Scheme 2. *Synthesis of the 5,5′-Bipyrimidines* **4a**–**c**



5-Aminouracil **1** **2**

3a R=Ph
3b R=Et
3c R=$C_{12}H_{25}$

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4b R=Et
4c R=$C_{12}H_{25}$

a) HCl (aq.), $NaNO_2$, 0°, then Cu powder, 60°; 43%. *b*) $POCl_3$, PCl_5, reflux; 56%. *c*) Bis(2,4-dimethoxybenzyl)amine, Et_3N, PhMe, reflux; 100%. *d*) For R = Ph: PhOH, K_2CO_3, 150°; 78%; for R = Et: EtOH, EtONa, reflux; 87%. For R = $C_{12}H_{25}$: $C_{12}H_{25}OH$, Na, $PhCH_3$, 100°; 92%. *e*) DDQ, H_2O, $CHCl_3$, r.t.; R = Ph: 62%; R = Et: 68%; R = $C_{12}H_{25}$; 73%. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

4. Solid-State Structure Analysis. – The self-assembly of the molecular components **4a**, **4b**, and **4c** in the solid state was studied by determination of their crystal structures. Compound **4a** crystallized readily from PhCl and 1,2-dichloroethane, each solvent providing a different crystalline polymorph. In the case of PhCl, face-to-edge π-

stacking interactions involving the solvent and PhO groups of **4a** influence the mode of H-bonding. A 'double-ribbon' with peripherally disposed PhO groups, a motif intermediate between forms **B** and **C**, described in *Fig. 1*, is obtained (*Fig. 2*).

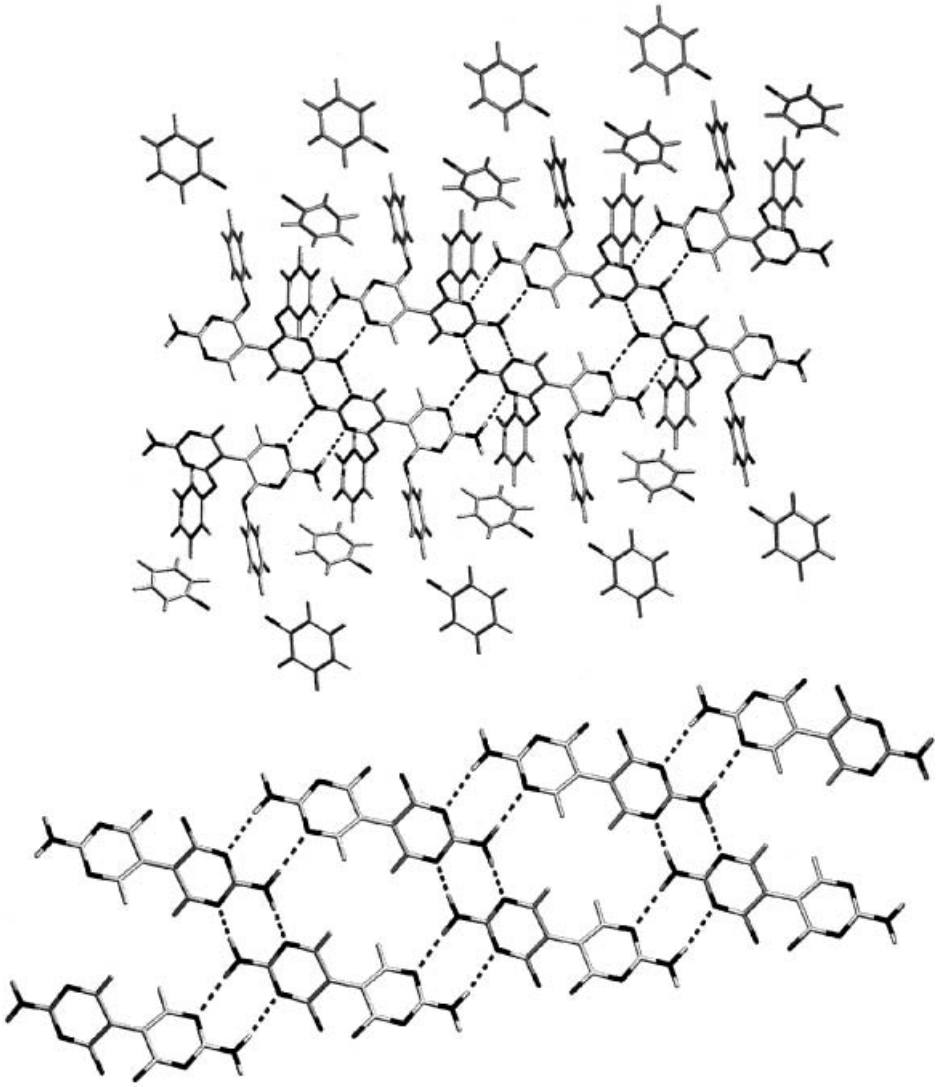

Fig. 2. *X-Ray crystal structure of* **4a** *crystallized from PhCl.* Top: *full structure*; bottom: *solvent molecules and PhO groups omitted for clarity.*

In contrast to the '*syn*'-arrangement observed for the substituents of the PhCl polymorph, the polymorph obtained from 1,2-dichloroethane assembles such that the PhO groups are in a *trans*-disposition as in motif **A** (*Fig. 1*). However, unlike motif **A**, the ribbon is derived from the H-bonding between the faces of the aminopyrimidine proximal to the PhO group (*Fig. 3*).

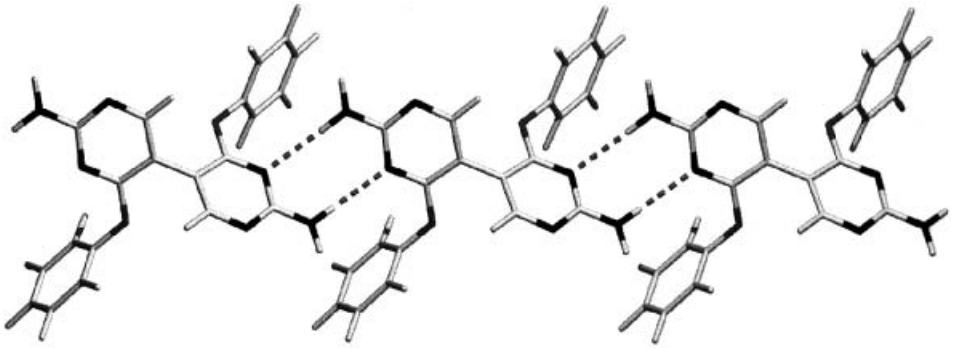

Fig. 3. *X-Ray crystal structure of* **4a** *crystallized from 1,2-dichloroethane* (solvent molecules omitted)

An unusual aspect for both polymorphs of **4a** involves highly angular H-bonds [9]. The NH···N H-bond geometry, implied from the angle between the participating pyrimidines, for the case of the PhCl polymorph, is 125°, and that for the 1,2-dichloroethane polymorph is 115°. These NH···N geometries differ remarkably from the average value of 160° [10].

Interestingly, and in contrast to the 1,2-dichloroethane polymorph of **4a**, the EtO-substituted compound **4b** yields a H-bonded ribbon, exactly as described for motif **A** (*Fig. 1*), involving H-bonding between the faces of the 2-aminopyrimidine distal to the alkoxy substituent (*Fig. 4*).

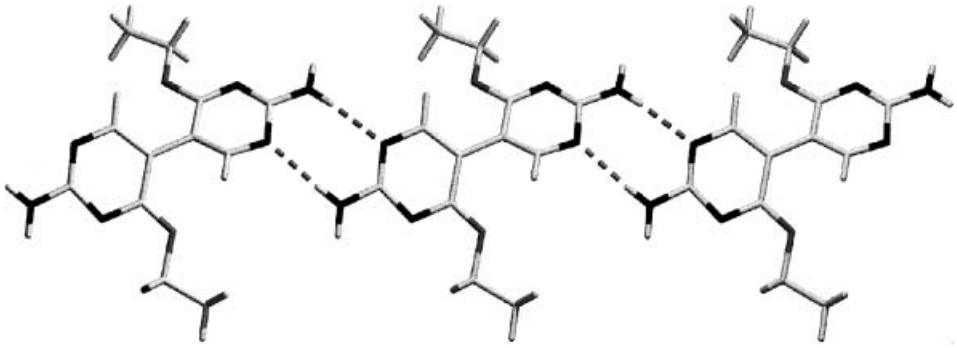

Fig. 4. *X-Ray crystal structure of 4,4′-diethoxy-5,5′-bipyrimidine* **4b**

Upon extending the alkyl chain from EtO, as in **4b**, to dodecyloxy, as in **4c**, one may observe the layered segregation of hydrophobic and hydrophilic residues in the lattice (*Fig. 5*). A surface, as depicted for motif **C** (*Fig. 1*), is generated (*Fig. 5*, center). That all H-bonds of the dodecyloxy derivative **4c** are satisfied, as opposed to the related EtO derivative **4b**, suggests the importance of a hydrophobic environment in promoting strong H-bonds in the solid state and, as a consequence, dominance of the H-bonding interactions in the determination of the assembly pattern.

The viabilty of using H-bonded networks as scaffolds to control the relative spatial orientation of functional residues requires not only a well-defined H-bonding motif, but a facile and modular means of appending the functional residues. Herein, we have

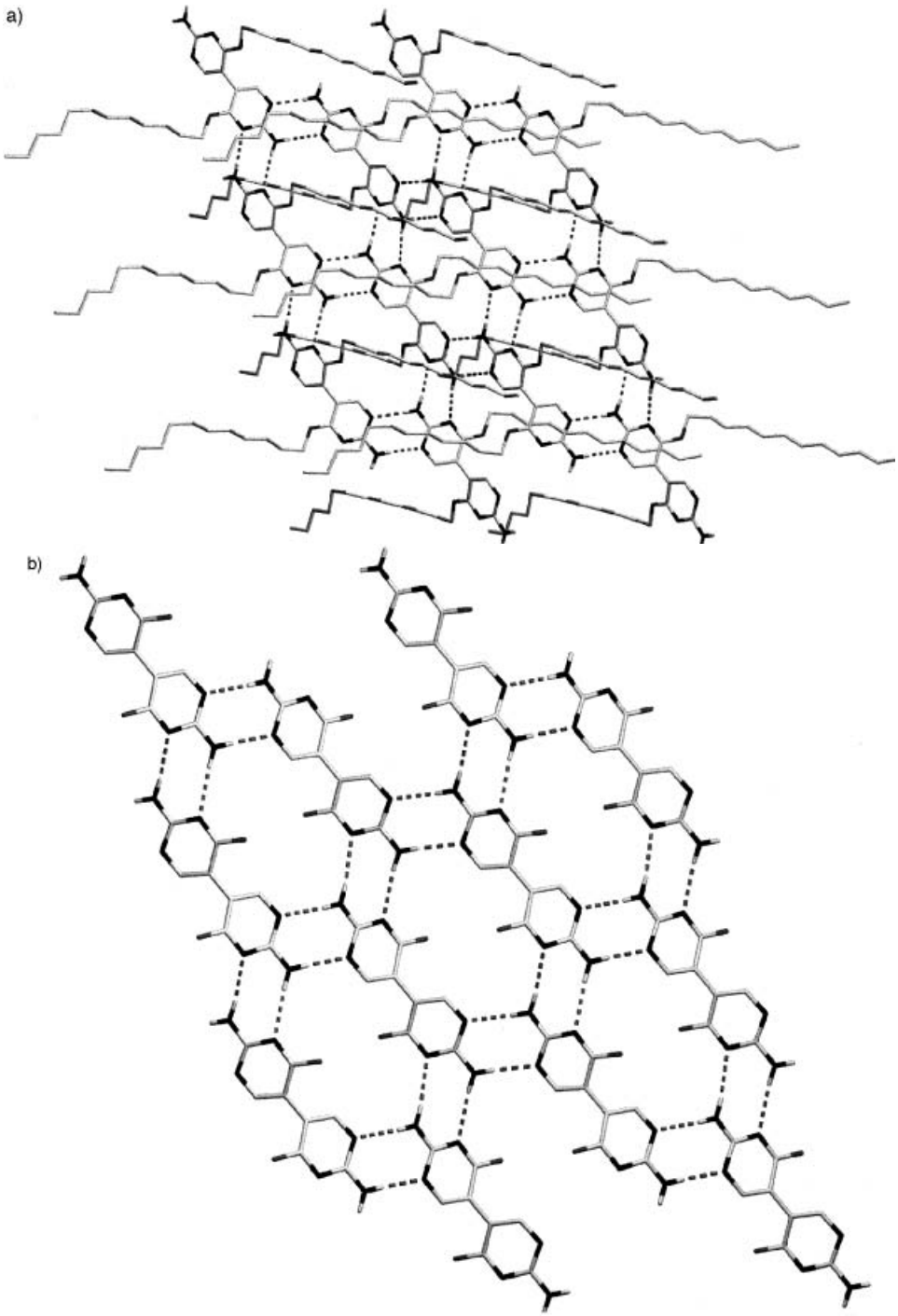

Fig. 5. *X-Ray crystal structure of 4,4′-didodecyloxy-5,5′-bipyrimidine* **4c**. a) *Full structure*; b) *alkyl chains omitted for clarity*; c) *space-filling representation of the layering of hydrophobic and hydrophobic residues.*

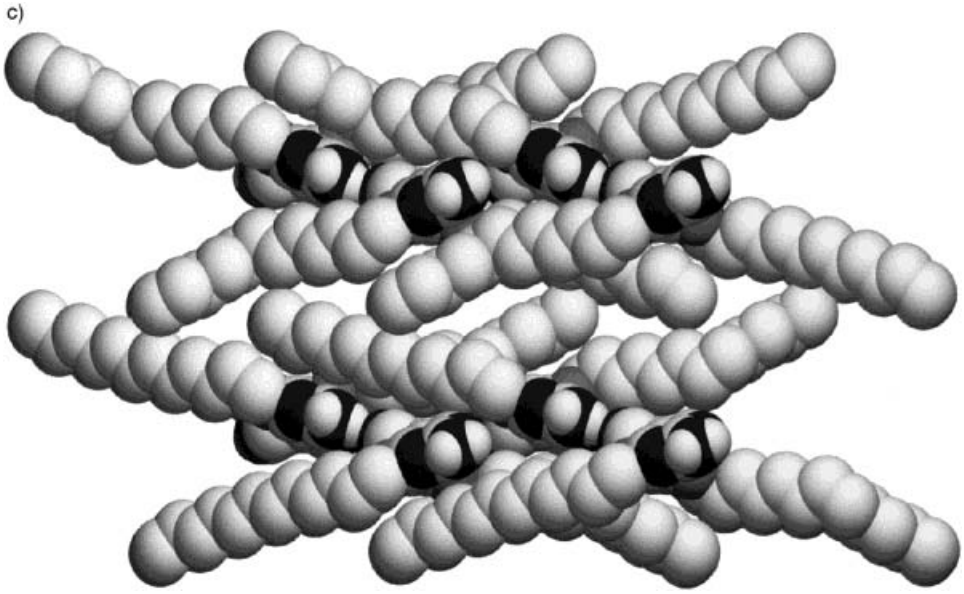

Fig. 5 (cont.)

explored the utility of 2,2′-diamino-4,4′-dialkoxy-5,5′-bipyrimidines as a scaffold for the modular introduction of 4,4′-dialkoxy substitution. Probing the influence of aromatic (**4a**), short-chain aliphatic (**4b**), and long-chain aliphatic residues (**4c**), an interesting result emerges regarding the promotion of H-bonds in the solid state. It appears that, while substituent size may sterically inhibit the approach of two H-bonding units, long aliphatic groups create a nonpolar environment that energetically drives H-bond formation. Comparison of the solid-state structures of **4b** and **4c** illustrates such control. Though the dodecyloxy side chains of **4b** are sterically more demanding than the EtO side chains of **4c**, all H-bonds of **4c** are satisfied, and a two-dimensional network results. For **4b**, only half of the H-bonds are satisfied resulting in the formation of a one-dimensional network.

The development of a useful paradigm for molecular-recognition-based self-assembly rests on the ability to identify and to adequately manipulate the dominant supramolecular interactions. In the specific case of H-bonded molecular solids, the influence of steric/*van der Waals*, π-stacking, and H-bonding information is well-established. Adding to this list, the present results stress the importance of hydrophobicity for the promotion of H-bonds in the solid state. The synergistic implementation of these collective factors to the engineering of the organic solid state should allow for control in the design of self-assembled functional materials. Future objectives may involve the introduction of conducting, push-pull conjugated, or odd-electron residues to the H-bonded scaffolds described herein as an approach to self-organized materials endowed with novel electrical, optical, or magnetic properties.

We thank the *NIH* for a post-doctoral fellowship (*M.J.K.*), and *A. Krische* for her expert help in generating the figure graphics.

Experimental Part

General. ^{1}H-NMR-Spectra: *Bruker SY 200* spectrometer at 200 MHz. ^{13}C-NMR Spectra: *Bruker SY 200* spectrometer or *Bruker ARX* 500-MHz spectrometer, at 50.3 and 125.72 MHz, resp.; solvent was used as an internal reference for both ^{1}H- and ^{13}C-NMR spectra. IR Spectra: *Perkin-Elmer 1600* Series FTIR instrument. M.p.: electrothermal digital melting-point apparatus; uncorrected. EI- and FAB-MS: by the Service de Spectrometrie de Masse, Institut de Chimie, Université Louis Pasteur. Purchased reagents were used without purification. Toluene was distilled from Na metal under dry N_2. CH_2Cl_2 was distilled from CaH_2 under dry N_2.

2,2′-Bis[(2,4-dimethoxybenzyl)amino]-4,4′-dichloro-5,5′-bipyrimidine (**2**). To a flask charged with *2,2′,4,4′-tetrachloro-5,5′-bipyrimidine* (**1**; 1.83 g, 6.2 mmol, 100 mol-%), a toluene soln. (62 ml, 0.1M) of bis(2,4-dimethoxybenzyl)amine (4.93 g, 15.5 mmol, 250 mol-%) was added, followed by Et_3N (4.33 ml, 31 mmol, 500 mol-%). The soln. was gently refluxed for 2.5 h. Then, it was allowed to cool and was partitioned between $CHCl_3$ and H_2O. The aq. phase was extracted with $CHCl_3$, and the combined org. layers were dried (Na_2SO_4), filtered, and evaporated. Chromatographic purification of the residue (SiO_2; AcOEt/hexane 35:65) gave **2** (5.64 g) in quant. yield. Clear, viscous oil. IR (film): 2999, 2936, 2836, 1613, 1582, 1505, 1464, 1417, 1364, 1288, 1257, 1208, 1157, 1127, 1037, 934, 832, 786. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.17 (*s*, 2 H); 7.15 (*m*, 4 H); 6.47 (*m*, 8 H); 4.88 (*s*, 6 H); 4.62 (*s*, 2 H); 3.82 (*s*, 6 H); 3.80 (*s*, 6 H); 3.79 (*s*, 6 H); 3.76 (*s*, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 161.5; 160.5; 160.2; 159.8; 158.4; 129.5; 128.2; 121.7; 118.0; 115.2; 103.7; 103.6; 98.4; 98.2; 61.3; 55.2; 54.9; 45.2. EI-MS: Calc. for $C_{44}H_{48}Cl_2N_6O_8$ ($[M+1]^+$): 857.2832; found: 857.2. Anal. calc. for $C_{44}H_{48}Cl_2N_6O_8$ (856.28): C 61.56, H 5.41; found: C 61.56, H 5.26.

2,2′-Bis[(2,4-dimethoxybenzyl)amino]-4,4′-diphenoxy-5,5′-bipyrimidine (**3a**). A flask charged with **2** (5.64 g, 6.57 mmol, 100 mol-%), phenol (8.76 g, *ca*. 0.75M upon liquification), and K_2CO_3 (3.63 g, 26.3 mmol, 400 mol-%) was placed in a 150° oil bath and stirred for 2.5 h. The mixture was allowed to cool and was partitioned between $CHCl_3$ and 1M NaOH. The org. layer was washed three times with 1M NaOH, dried ($MgSO_4$), filtered, and evaporated. Chromatographic purification of the residue (SiO_2; AcOEt/hexane 35:65) gave **3a** (4.98 g) as a clear, viscous oil, in 78% yield. IR (film): 3005, 2936, 2834, 1602, 1504, 1463, 1415, 1347, 1289, 1255, 1208, 1156, 1118, 1038, 974, 912, 833, 755, 691. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.35 (*s*, 2 H); 7.10–7.35 (*m*, 10 H); 6.67 (br. *d*, $J=7.4$, 2 H); 6.39 (br. *m*, 10 H); 4.90 (br. *s*, 4 H); 4.45 (br. *s*, 4 H); 3.85 (*s*, 18 H); 3.65 (br. *s*, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 166.5; 161.3; 159.5; 159.4; 158.3; 153.0; 129.6; 128.8; 128.0; 124.4; 122.1; 118.9; 103.5; 103.3; 98.1; 55.2; 54.9; 45.6. EI-MS: Calc. for $C_{56}H_{56}N_6O_{10}$ ($[M+1]^+$): 973.4136; found: 973.3.

2,2′-Bis[(2,4-dimethoxybenzyl)amino]-4,4′-diethoxy-5,5′-bipyrimidine (**3b**). Na metal (1.26 g, 55 mmol, 1000 mol-%) was added portionwise to EtOH (27 ml) at 0°. The resultant ethanolic EtONa soln. was added to a soln. of **2** (4.72 g, 5.50 mmol, 100 mol-%) in toluene (27 ml, 0.2M), and the soln. was gently refluxed for 20 h. The mixture was allowed to cool and was partitioned between $CHCl_3$ and brine. The aq. layer was extracted once with $CHCl_3$, and the combined org. layers were dried (Na_2SO_4), filtered and evaporated. Chromatographic purification of the residue (SiO_2; AcOEt/CH_2Cl_2 4:96) gave **3b** (4.19 g), as a clear, viscous oil, in 87% yield. IR (film): 2936, 2835, 1587, 1504, 1416, 1348, 1287, 1208, 1156, 1118, 1036, 977, 916, 833, 793, 733, 647. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.22 (*s*, 2 H); 7.18 (*d*, $J=8.1$, 4 H); 6.48 (*m*, 8 H); 4.90 (*s*, 8 H); 4.32 (*q*, $J=7.1$, 4 H); 3.78 (*s*, 12 H); 3.77 (*s*, 12 H); 1.26 (*t*, $J=7.0$, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 166.2; 161.2; 159.5; 158.2; 128.2; 119.0; 103.6; 103.2; 98.0; 61.3; 55.0; 54.9; 44.7; 14.2. EI-MS: Calc. for $C_{48}H_{56}N_6O_{10}$ ($[M+1]^+$): 877.4136; found: 877.8.

2,2′-Bis[(2,4-dimethoxybenzyl)amino]-4,4′-didodecyloxy-5,5′-bipyrimidine (**3c**). To a soln. of $C_{12}H_{25}OH$ (11.5 g, *ca*. 0.2M upon liquification) in toluene (11.5 ml, 0.2M), Na metal (266 mg, 23.3 mmol, 1000 mol-%) was added. Upon complete consumption of the metal, a toluene soln. (11.5 ml, 0.2M) of **2** (2.0 g, 2.33 mmol, 100 mol-%) was added, and the soln. was stirred at 120° for 24 h. The mixture was allowed to cool and was partitioned between $CHCl_3$ and brine. The aq. layer was extracted once with $CHCl_3$, and the combined org. layers were dried (Na_2SO_4), filtered, and evaporated. Chromatographic purification of the residue (SiO_2; AcOEt/hexane 10:90 → 40:60) gave **3c** (2.49 g), as a clear, viscous oil, in 92% yield. IR (film): 2924, 2852, 1613, 1587, 1504, 1463, 1415, 1349, 1286, 1253, 1207, 1155, 1118, 1039, 831, 793. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 2 H); 7.14 (*d*, $J=8.8$, 4 H); 6.45 (*m*, 8 H); 4.84 (*s*, 8 H); 4.22 (*t*, $J=6.8$, 4 H); 3.80 (*s*, 12 H); 3.76 (*s*, 12 H); 1.65 (br. *m*, 4 H); 1.27 (*m*, 36 H); 0.90 (*t*, $J=5.8$, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 166.4; 161.2; 159.5; 158.2; 128.2; 119.1; 103.5; 103.3; 98.1; 65.7; 55.0; 54.9; 44.8; 31.7; 29.5; 29.2; 28.6; 25.8; 22.5; 13.9. EI-MS: Calc. for $C_{68}H_{96}N_6O_{10}$ ($[M+1]^+$): 1157.7265; found: 1157.6.

2,2′-Diamino-4,4′-diphenoxy-5,5′-bipyrimidine (**4a**). To a vigorously stirred soln. of **3a** (4.25 g, 4.36 mmol, 100 mol-%) in $CHCl_3/H_2O$ 20:1 (145 ml, 0.03M) at r.t., DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone; 5.9 g,

26.1 mmol, 600 mol-%) was added. The mixture was stirred for 8 h. Then, it was partitioned between $CHCl_3$ and 1M NaOH. The org. layer was washed three times with 1M NaOH, dried ($MgSO_4$), filtered, and evaporated onto silica. Chromatographic purification (SiO_2; EtOH/AcOEt 5:95) gave **4a** (1.00 g), as beige powder, in 62% yield. Compound **4a** may be crystallized by slow evaporation from $CHCl_3$, 1,2-dichloroethane, or PhCl. M.p. 255–256°. IR (film): 3333, 1595, 1545, 1462, 1416, 1230. ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.18 (*s*, 2 H); 7.37 (*t*, *J* = 7.4, 4 H); 7.18 (*t*, *J* = 7.4, 2 H); 7.08 (*d*, *J* = 7.4, 4 H); 6.66 (*s*, 4 H). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 166.6; 162.8; 159.7; 152.8; 129.4; 124.7; 121.5; 103.6. EI-MS: Calc. for $C_{20}H_{16}N_4O_2$ (M^+): 344.1273; found: 344.2.

2,2′-Diamino-4,4′-diethoxy-5,5′-bipyrimidine (**4b**). The compound **4b** (659 mg) was prepared in 68% yield from **3b** (3.08 g, 3.51 mmol, 100 mol-%) by the same protocol as described for **4a**. Compound **4b** may be recrystallized by slow evaporation from 1,2-dichloroethane. M.p. 216–217°. IR (film): 3330, 1620, 1583, 1537, 1417, 1375, 1326, 1031, 985, 795. ^{1}H-NMR (200 MHz, (D_6)DMSO): 7.84 (*s*, 2 H); 6.51 (*s*, 4 H); 4.28 (*q*, *J* = 7.04, 4 H); 1.22 (*t*, *J* = 7.04, 6 H). ^{13}C-NMR (50.3 MHz, (D_6)DMSO): 166.3, 162.5, 157.9, 103.6, 60.8, 14.3. EI-MS: Calc. for $C_{12}H_{16}N_6O_2$ (M^+): 276.1335; found: 276.3.

2,2′Diamino-4,4′-didodecyloxy-5,5′-bipyrimidine (**4c**). The compound **4c** (393 mg) was prepared in 73% yield from **3c** (1.12 g, 0.967 mmol, 100 mol-%) by the same protocol as described for **4a**. Compound **4c** may be recrystallized by slow evaporation from $CHCl_3$. M.p. 156°. IR (film): 3400, 3250, 2919, 1651, 1585, 1543, 1479, 1415, 1349, 1241, 1031, 987, 798, 722. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.98 (*s*, 2 H); 5.01 (br. *s*, 4 H); 4.27 (*t*, *J* = 6.7, 4 H); 1.68 (*m*, 4 H); 1.25 (*m*, 36 H); 0.83 (*t*, *J* = 6.0, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 167.5; 162.1; 158.4; 105.7; 66.4; 32.0; 29.7; 29.4; 28.7; 26.0; 22.8; 14.2. EI-MS: Calc. for $C_{32}H_{56}N_6O_2$ ($[M+1]^+$): 557.4542; found: 557.5.

Crystal Data for **4a** (from 1,2-dichloroethane): $C_{22}H_{20}N_6O_2Cl_2$, M_r 471.35, monoclinic, space group *C*2/*c*, $a = 12.479(2)$, $b = 19.746(2)$, $c = 10.126(2)$ Å, $\beta = 109.63(1)°$, $V = 2350(1)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.33$ g cm^{-3}, $\mu(MoK_\alpha) = 0.304$ mm^{-1}. Colorless crystal of dimensions $0.40 \times 0.20 \times 0.20$ mm^3. 2609 reflections collected, $2.5° < \theta < 26.28°$. 1216 independant reflections having $I > 3\sigma(I)$. Transmission coefficients min/max: 0.96/1.00. 144 parameters. Final results: $R(F) = 0.053$, $Rw(F) = 0.081$, $GOF = 1.631$, maximum residual electronic density = 0.35 e Å^{-3}.

Crystal Data for **4a** (from PhCl): $C_{32}H_{26}N_6O_2Cl_2$, M_r 597.51, monoclinic, space group $P2_1/c$, $a = 9.935(1)$, $b = 13.859(2)$, $c = 21.630(2)$, $\beta = 92.30(1)°$, $V = 2976(1)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.33$ g cm^{-3}, $\mu(MoK_\alpha) = 0.255$ mm^{-1}. Colorless crystal of dimensions $0.35 \times 0.16 \times 0.12$ mm^3. A total of 6253 reflections, $2.5° < \theta < 26.30°$. 2456 reflections having $I > 3\sigma(I)$. Transmission coefficients min/max: 0.94/1.00. Final results: $R(F) = 0.081$, $Rw(F) = 0.089$, $GOF = 1.016$, maximum residual electronic density = 0.21 e Å^{-3}. In common: *Nonius CAD4-MACH3* diffractometer, MoK_α graphite monochromated radiation ($\lambda = 0.71073$ Å), $\omega/2\theta$ scans, r.t. Absorption corrections from psi-scans. The structures were solved using direct methods and refined against $|F|$. H-Atoms were introduced as fixed contributors. For all computations the *Enraf-Nonius* MolEN package was used.

Crystal Data for **4b**: $C_{12}H_{16}N_6O_2$, M_r 276.31, monoclinic, space *Cc* (No. 9), $a = 9.761(7)$, $b = 14.521(6)$, $c = 10.215(1)$ Å, $\beta = 109.04(3)°$, $V = 1369(1)$ Å^3, $F(000) = 584$, $\mu(MoK_\alpha) = 0.097$ mm^{-1}, $T = 173 \pm 1$ K, $Z = 4$, $D_c = 1.341$ g cm^{-3}. Data were recorded with an *Enraf-Nonius CAD4* diffractometer using graphite monochromatized. MoK_α radiation ($\lambda = 0.71073$ Å) and a $\omega/2\theta$ scan mode. 1346 reflections were recorded in the range $2.62 < \theta < 24.92$ of which 1287 were unique. Reflections were corrected for *Lorentz*-polarization effects and *y*-scan method was used for absorption correction (maximum transmission 0.9952 and minimum transmission 0.9443). The structure was solved by direct methods and refinement, based on F^2, was by full-matrix least-squares techniques [11]. The H-atoms were calculated to their idealized geometric positions with isotropic temp. factors (1.2 or 1.5 times the C temp. factor) and were refined as riding atoms. The temp. factor of C6 was restrained (EADP) to a reasonable value by equalizing it with the temperature factor of C6′. The final residuals were $R1 = 0.0494$ and $wR2 = 0.1152$ for 721 unique data with $I > 2\sigma(I)$ and $R1 = 0.1065$, $wR2 = 0.1354$ (all data). $GooF = 0.916$. The compound crystallized in an acentric space group due to the spontaneous resolution and due to the small anomalous dispersion effects the absolute configuration could not be determined.

Crystal Data for **4c**: $C_{32}H_{56}N_6O_2$, M_r 556.83, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.064(3)$, $b = 25.425(4)$, $c = 13.731(4)$ Å, $\beta = 108.96(2)°$, $V = 3323(2)$ Å^3, $F(000) = 1224$, $\mu(MoK_\alpha) = 0.070$ mm^{-1}, $T = 173 \pm 1$ K, $Z = 4$, $D_c = 1.113$ g cm^{-3}. Data were recorded with an *Enraf-Nonius CAD4* diffractometer using graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and a $\omega/2\theta$ scan mode. 6195 reflections were recorded in the range $2.20 < \theta < 25.00$ of which 5845 were unique ($R_{int} = 0.037$). Reflections were corrected for *Lorentz*-polarization effects and *y*-scan method was used for absorption correction (maximum transmission 0.9802 and minimum transmission 0.9184). The structure was solved by direct methods and refinement, based on F^2, was by full-matrix least-squares techniques [11]. The H-atoms were calculated to their idealized geometric positions with isotropic temp. factors (1.2 or 1.5 times the C temp. factor) and were refined as riding atoms. The final

residuals were $R1 = 0.0837$ and $wR2 = 0.1714$ for 1829 unique data with $I > 2\sigma(I)$ and $R1 = 0.2421$, $wR2 = 0.2123$ (all data). $GooF = 0.837$.

Crystallographic data (excluding structure factors) for all structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre*. Further details of the crystal-structure investigations are available on request from the Director of *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the full journal citation.

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Received August 17, 1998