Molecular Ribbons from Molecular Recognition directed Self-assembly of Self-complementary Molecular Components

Jean-Marie Lehn,*[a] Mark Mascal,†[a] André DeCian[b] and Jean Fischer[b]
[a] *Laboratoire de Chimie Supramoléculaire, URA 422 of the CNRS*
[b] *Laboratoire de Cristallochimie, URA 424 of the CNRS, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France*

The programmed self-association of the self-complementary nucleotide-like pyrimidinone **5** and pyrimidinedione **6**, generates, as predicted, organized supramolecular ribbons. The crystal structure of such a species has been determined. A similar entity is obtained from the pyrimidinetriamine **12** with solvent participation, giving a quadruply hydrogen-bonded ribbon, whose crystal structure has also been determined. These processes give access to the designed generation of organized arrays of functional substituents.

The basis of molecular recognition is the presence of information in the interacting components. In supramolecular assemblies, information is expressed by a component's potential for entering into non-covalent bonding relationships with its partners and by its steric requirements. An overall reckoning of attractive and repulsive interactions may lead to a unique solution at a free-energy minimum for a given system. From a practical point of view, the large number of variables which have to be addressed, *i.e.* the magnitude and direction of the non-covalent interactions involved, makes this a non-trivial task in multicomponent systems. Thus, most studies of molecular recognition directed self-assembly have been based on hydrogen bonding, metal–ligand, and/or aromatic stacking interactions, since the geometry of these interactions is often predictable.

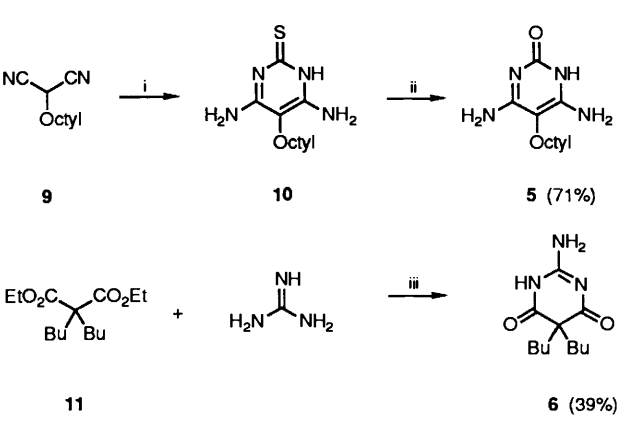
Knowledge of these parameters allows the design of systems of programmed components[1] capable, in principle, of undergoing self-organization into a given supramolecular architecture. Such components must contain the necessary molecular information as well as the interaction algorithm for reading it.[1]

As part of a general investigation of self-assembly in hydrogen bonding systems[2] we recently reported[3] on the cocrystallization of two hetero-complementary molecular components which were designed to generate a polymeric strand displaying spontaneous molecular sorting with left-/right-hand differentiation.[4] We now describe the design and synthesis of some *self*-complementary hydrogen-bonding recognition units.

In the previous work,[3] complementary 5,5-diethylbarbituric acid (**1**) and 5-butylpyrimidine-2,4,6-triamine (**2**) subunits were prepared, each of which presented two identical binding faces (Fig. 1). Full use of the hydrogen-bonding potential should lead to the formation of three hydrogen bonds between the binding sites of the complementary partners. Indeed, when solutions of the two were mixed, the rapid precipitation of a hydrogen-bonded complex was observed. The nature of this complex was ascertained by determination of its crystal structure. The information possessed by these symmetrical components could generate two independent geometric expressions: a ribbon-like polymeric motif **3** or a cyclic hexamer **4** (Fig. 1). X-Ray crystallography showed that **3** was actually formed under the conditions which were applied.[3]

Thus, we set about designing subunits in which this symmetry was broken, and which hence would be capable of only a *single* spatial relationship with neighbouring subunits—indeed 'better-informed' components. This was realized in the complementary pair 4,6-diamino-5-octylpyrimidin-2(1*H*)-one (**5**) and 2-amino-5,5-dibutylpyrimidine-4,6(1*H*)-dione (**6**), which are, at the same time, complementary to each other and *self*-complementary. The hetero-association of **5** with **6** could *only* lead to the expression of a macrocyclic ring **7** (Fig. 2), while the self-association of either **5** or **6** could *only* lead to ribbon polymers **8a,b** analogous to **3** in Fig. 1. It can be said that compounds **5** and **6** possessed, indeed were programmed with, a higher degree of information than **1** and **2**.

The synthesis of these compounds was straightforward. The obvious route of condensation of the appropriate synthon with either the corresponding malononitrile or malonic ester was, however, only successful for compound **6** (Scheme 1). The failure of urea to condense with octylmalononitrile (**9**) led us to turn to the more nucleophilic thiourea,[5] which gave the pyrimidinethione **10**, which in turn could be hydrolysed to **5**. Compounds **5** and **6** were white, crystalline solids whose poor solubility and high melting points (323–325 °C for **5**, 400 ± 5 °C for **6**) were evidence for strong self-association.



Scheme 1 *Reagents:* i, thiourea–NaOEt–EtOH, reflux; ii, aq. $ClCH_2CO_2H$, reflux, then H_2SO_4, reflux; iii, NaOEt–EtOH, reflux

Equimolar solutions of **5** and **6** in hot dimethylformamide (DMF) deposited, on being cooled, crystals containing only the less soluble compound **5**. Altering the concentration ratio to favour compound **6** did not result in cocrystallization, indeed crystals of pure **5** precipitated from solutions saturated in **6**. The crystal structure of compound **5** was determined and revealed, as predicted, a zig-zag polymeric motif, a supramolecular ribbon formed by a continuous array of heterocyclic units, each of which is linked by 2 × 3 hydrogen bonds to its two neigh-

† *Present address:* Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

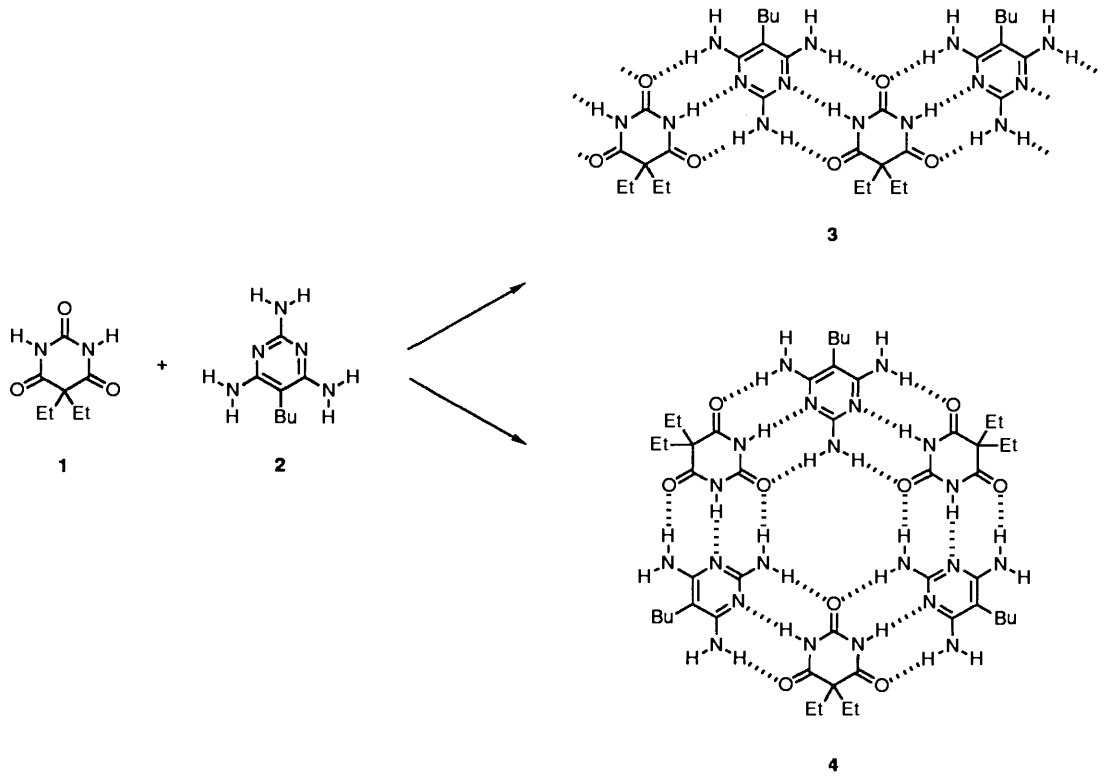


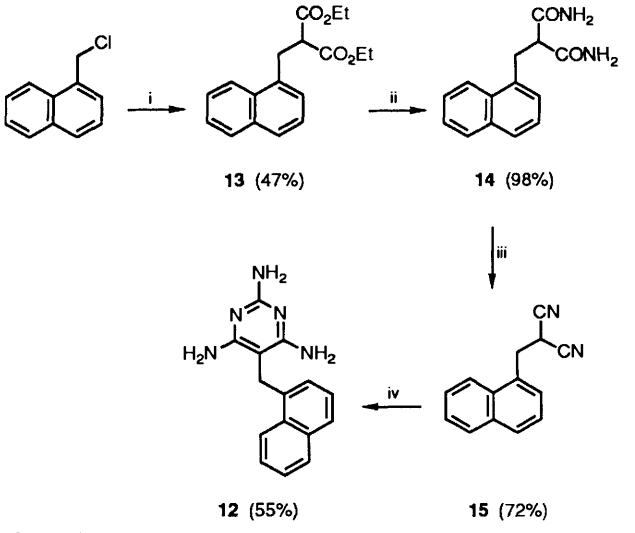
Fig. 1

bours. In addition the structure contains two molecules of DMF solvent per subunit. (Fig. 3). Preferred hydrogen bonding between identical rather than different components and low solubility of the resulting species is thus the governing factor for the solid-state structure of this system. Since the self-complementary hydrogen-bonded polymers are much less soluble than the cyclic hexamer is expected to be, the solid-state composition of a mixture of **5** and **6** is $\mathbf{5}_n + \mathbf{6}_n$ and not $(\mathbf{5}_3\mathbf{6}_3)_n$.

The hydrogen-bonding distances between the heterocyclic components (2.89 Å average) indicate strong interaction. The octyl chains are in a *tttgtt* conformation (starting from the ring core) and located at 9.68 Å intervals on the polymer backbone. The two DMF solvent molecules saturate the remaining hydrogen-bonding sites by interacting at each free N–H position through an N–H • • • O link (Fig. 3).

The components of the assembled system $(\mathbf{1}\cdot\mathbf{2})_n$ may also be considered self-complementary, but, with only two hydrogen bonds per binding face, the information is such that the precise nature of the self-association of **1** or **2** cannot be unambiguously predicted. Indeed, for compound **1**, the existence of six different polymorphs has been demonstrated,[6] three of which (forms **I**, **II** and **IV**) have been analysed by X-ray crystallography.[7,8] Forms **I** and **II** are flat chains (Fig. 4), while form **IV** is complex and not easily represented in two dimensions.

The crystal structure of the parent compound of **2**, *i.e.* pyrimidine-2,4,6-triamine has also been solved[9] (Fig. 5) and is similar to form **II** of compound **1** (Fig. 4). We have determined the crystal structure of the pyrimidinetriamine derivative, 5-(1-naphthyl)methylpyrimidine-2,4,6-triamine (**12**). It compares with that in Fig. 5, but involves the participation of solvent molecules (dimethyl sulfoxide) to bind remaining N–H sites, resulting in a broad ribbon based on a total of *eight* hydrogen bonds per subunit (Fig. 6). The full hydrogen-bonding pattern resembles that found in a *mismatched base pair* guanine–thymine GT in an oligonucleotide, where two water molecules bridge the mispaired bases, also forming an array of four hydrogen bonds between the two interacting groups.[10] Such a pattern also represents a sort of frame shift between the two units. Examination of the structure of $\mathbf{12}_n$ reveals that the naphthalene residues are arranged in parallel series on either side of the strand at a distance of 12.42 Å. This raises the intriguing possibility of observing long-range light-induced energy or electron transfer along the stacks of regularly spaced and parallel-oriented aromatic groups. Left/right interstack transfer could also occur. The cavities defined by the naphthyl groups are occupied by two Me_2SO molecules each of which forms two N–H • • • O hydrogen bonds with NH_2 groups of two neighbouring heterocycles. Compound **12** was prepared in four steps from 1-(chloromethyl)naphthalene as shown in Scheme 2.



Scheme 2 *Reagents*: i, diethyl malonate–NaOEt–EtOH, reflux; ii, NH_3–Na–MeOH; iii, P_2O_5, heat; iv, guanidinium•HCl–NaOEt–EtOH, reflux

Molecular programming involves the application of non-covalent 'design principles' to the synthesis of molecular com-

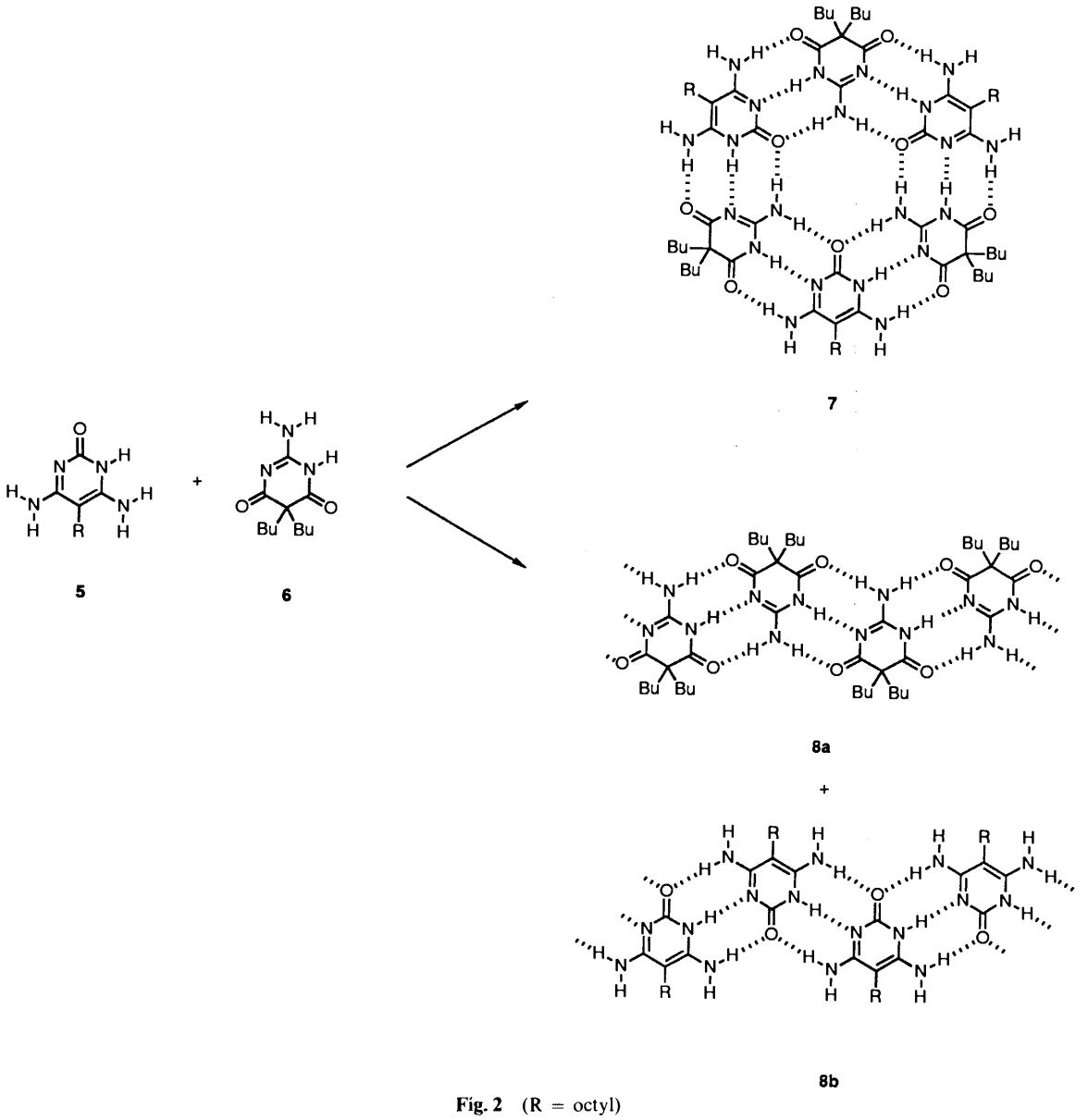


Fig. 2 (R = octyl)

ponents possessing a recognition algorithm whose operation leads to the desired supramolecular architecture. The directed interaction between two (or more) different complementary species, as well as that of self-complementary molecules, results in assemblies possessing short- or long-range order. The specific engineering of molecular components substituted with conducting, push–pull conjugated, or odd-electron residues may lead to functional self-organised organic materials presenting defined molecular patterns and networks and potentially endowed with novel electrical, optical or magnetic properties.

Experimental

General.—Melting points were determined on an Electrothermal digital melting-point apparatus. Proton NMR spectra were recorded on a Bruker AC 200 spectrometer and referenced to the residual protons of the solvents; shifts are given with respect to Me_4Si. *J* Values are in Hz. Electron impact or chemical ionization (CI) mass spectra were determined on a Finnigan TSQ 70 spectrometer.

Nonane-1,1-dicarbonitrile **9**.—To a mixture of malononitrile (13.21 g, 0.20 mol), *n*-octanal (28.00 g, 0.22 mol) and 5% palladium-on-charcoal (400 mg) in acetic acid (30 cm^3) was added a solution of piperidine (0.8 cm^3) in acetic acid (10 cm^3) and the whole was stirred vigorously under 1 atm of hydrogen for 18 h. The solvent and excess aldehyde were removed on a rotary evaporator and the residue was distilled at 1.0 Torr. The fraction collected between 115–120 °C was identified as the title compound **9** (23.52 g, 66%), and was used immediately without further purification. δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, br t, 9-H), 1.27 (10 H, br m, 4-, 5-, 6-, 7- and 8-H), 1.60 (2 H, m, 3-H), 2.02 (2 H, m, 2-H) and 3.70 (1 H, t, *J* 6.9, 1-H); *m/z* 177 (M − H, 14%), 163 (M − CH_3, 26), 149 (M − CH_2CH_3, 12), 135 [M − $(CH_2)_2CH_3$, 34], 122 (42), 108 (30), 94 (24), 82 (44), 69 (46), 57 ($C_4H_9^{+\bullet}$, 51), 55 ($C_4H_7^{+\bullet}$, 51), 54 (48), 43 ($C_3H_7^{+\bullet}$, 88) and 41 ($C_3H_5^{+\bullet}$, 100).

4,6-*Diamino-5-octylpyrimidine-2*(1H)-*thione* **10** *and* 4,6-*Diamino-5-octylpyrimidin-2*(1H)-*one* **5**.—A solution of sodium ethoxide was prepared from sodium (460 mg, 20.0 mmol) and absolute ethanol (15 cm^3). Nonane-1,1-dicarbonitrile (**9**) (3.57 g, 20.0 mmol) and thiourea (1.52 g, 20.0 mmol) were added and the mixture was heated at reflux for 2 h. Water (25 cm^3) was added and the reaction mixture was neutralized with dil. hydrochloric acid, causing the thiocytosine **10** to precipitate. This was collected on a filter and suspended in water (75 cm^3). Chloroacetic acid (5.0 g, 52.9 mmol) was added and the mixture was

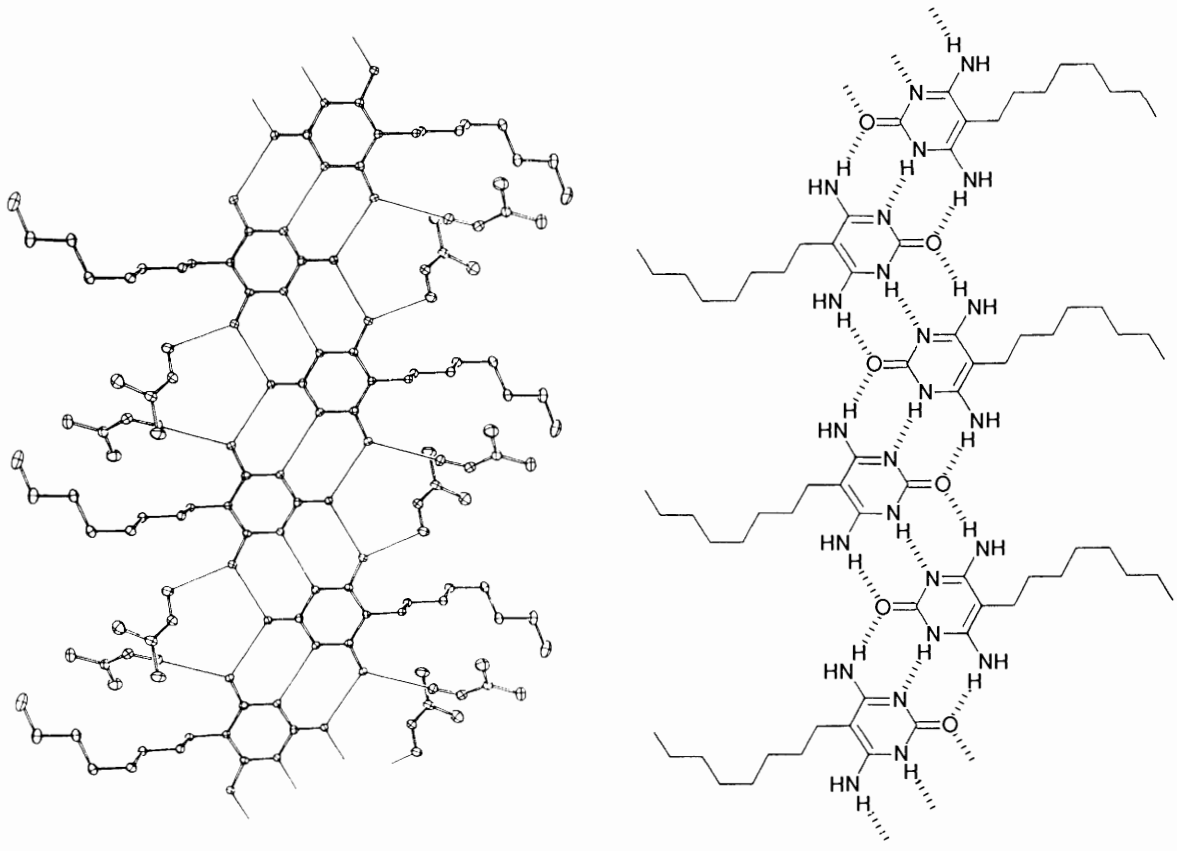
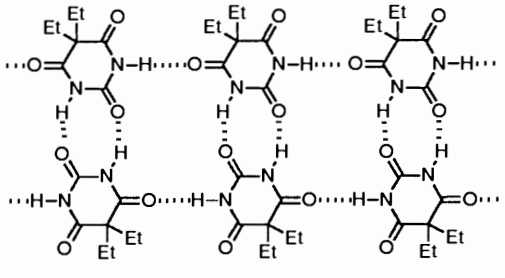
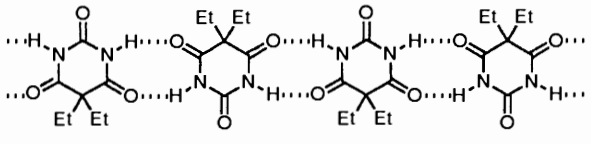


Fig. 3 X-Ray structure of the hydrogen-bonded, ribbon-like species formed by self-assembly of the self-complementary component **5**. The schematic representation (right) omits the two DMF molecules contained in each cavity between the octyl chains.



Form I



Form II

Fig. 4

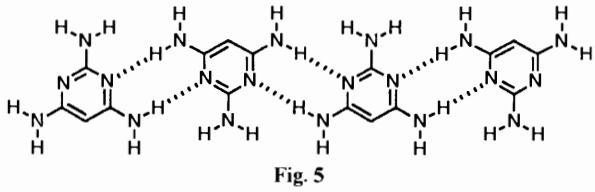


Fig. 5

heated at reflux for 90 min, to give a clear solution. Sulfuric acid (9 cm^3) was then carefully added without interrupting the reflux, causing the solution to become cloudy. After 1 h the reaction was removed from the heating bath and when the mixture had cooled to room temperature a precipitate was observed. This was filtered off to give the sulfate salt of the title compound. The free base was obtained by suspending the salt in saturated aq. sodium hydrogen carbonate at 70 °C with vigorous stirring for 10 h. The filtered title compound **5** (3.39 g, 71%) was a highly insoluble, white solid of m.p. 323–325 °C (with gas evolution); δ_H[200 MHz; $(CD_3)_2SO$] (sulfate salt of **5**) 0.85 (3 H, br t, CH_3), 1.24 [12 H, br s, $(CH_2)_6CH_3$], 2.21 (2 H, br m, $ArCH_2$) and 7.43 (4 H, br s, NH_2); *m/z* (CI) 267 (M + C_2H_5, 20%), 253 (M + CH_3, 5), 239 (MH^+, 100), 223 (M − CH_3, 4), 183 (8), 139 (M − C_7H_{15}, 72) and 122 (9).

Diethyl Dibutylmalonate **11**.—A solution of sodium ethoxide was prepared from sodium (5.75 g, 0.25 mol) and absolute ethanol (125 cm^3) to which was added diethyl butylmalonate (50.0 g, 50.9 cm^3, 0.23 mol) followed by 1-bromobutane (34.3 g, 29.6 cm^3, 0.25 mol). After a short induction period, a mildly exothermic reaction was observed accompanied by the formation of a white precipitate (sodium bromide). After the spontaneous reflux had subsided, the mixture was heated and held at reflux for 24 h. The reaction was cooled, filtered, and evaporated until no ethanol remained, then fractionally distilled at 10 Torr. The title compound **11** (39.57 g, 63%), was collected as a colourless liquid b.p. 125–126 °C (lit.,[11] b.p. 151–152 °C at 18 Torr); δ_H(200 MHz; $CDCl_3$) 0.88 (6 H, t, *J* 7.1, $CH_2CH_2CH_2CH_3$), 1.12 (4 H, m, $CH_2CH_2CH_2CH_3$), 1.22 (6 H, t, *J* 7.1 Hz, OCH_2CH_3), 1.28 (4 H, m, $CH_2CH_2CH_2CH_3$), 1.85 (4 H, m, $CH_2CH_2CH_2CH_3$) and 4.16 (4 H, q, *J* 7.1, OCH_2CH_3).

2-*Amino*-5,5-*dibutylpyrimidine*-4,6(1H)-*dione* **6**.—A solution of sodium ethoxide was prepared from sodium (382 mg, 16.6 mmol) and absolute ethanol (15 cm^3). Diethyl dibutylmalonate (**11**) (2.72 g, 10.0 mmol) and guanidine hydrochloride (1.06 g, 11.1 mmol) were added and the mixture was heated at reflux for

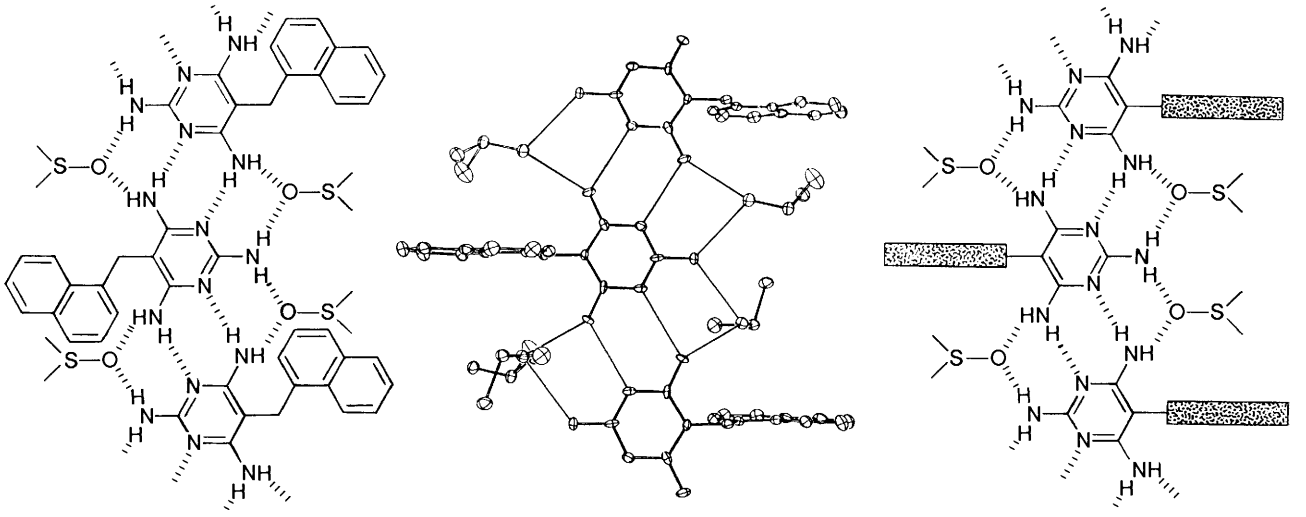


Fig. 6 X-Ray structure of the hydrogen-bonded species formed by self-assembly of the component **12** complemented by Me_2SO molecules; (left and right): schematic representations of the structure

8 h, then evaporated to dryness. Water (25 cm^3) was added to give momentarily a clear solution which quickly deposited a flocculent white precipitate. Dilute hydrochloric acid was added until the mixture was neutral and the product was collected on a filter and washed several times with ether to yield 940 mg (39%) of the title compound **6** in the form of a white powder which decomposed with gas evolution at 400 °C; δ_H[200 MHz; $(CD_3)_2SO$] 0.76 (6 H, t, *J* 7.1, $CH_2CH_2CH_2CH_3$), 0.92 (4 H, br m, $CH_2CH_2CH_2CH_3$), 1.10 (4 H, quintet, *J* 6.9, $CH_2CH_2CH_2CH_3$), 1.57 (4 H, br m, $CH_2CH_2CH_2CH_3$) and 7.30 (2 H, v br, NH_2); *m/z* (CI) 268 ($M + C_2H_5$, 18%), 240 (MH^+, 100), 238 (M − H, 13), 224 (M − CH_3, 7), 183 (M − C_4H_8, 33) and 140 (22).

Diethyl 1-Naphthylmethylmalonate **13**.—A solution of sodium ethoxide was prepared from sodium (3.45 g, 0.150 mol) and absolute ethanol (75 cm^3). Diethyl malonate (24.8 g, 23.6 cm^3, 0.155 mol) and 1-(chloromethyl)naphthalene (26.5 g, 0.150 mol) were added and the mixture was refluxed spontaneously for about 30 min, after which it was immersed in a heating bath and refluxed for an additional hour. The solvent was evaporated and water (100 cm^3) and chloroform (100 cm^3) were added. The mixture was shaken and the layers were separated. The aqueous layer was extracted with chloroform and the combined organic extracts were dried over sodium sulfate and evaporated. The residual liquid was distilled at 0.5 Torr and the title compound **13** (21.11 g, 47%) was collected between 165–167 °C (lit.,[12] b.p. 221 °C at 11 Torr) in the form of a highly viscous, pale yellow oil; $\delta_H(CDCl_3)$ 1.18 (6 H, t, *J* 7.1, OCH_2CH_3), 3.69 (2 H, m, $ArCH_2CH$), 3.83 (1 H, dd, *J* 6.4 and 8.5, $ArCH_2CH$), 4.15 (4 H, q, *J* 7.1, OCH_2CH_3), 7.36 (1 H, d, *J* 5.3, Ar-H), 7.51 (2 H, m, Ar-H), 7.74 (2 H, m, Ar-H), 7.85 (1 H, m, Ar-H) and 8.03 (1 H, d, *J* 8.4, Ar-H); *m/z* 300 (M^+, 73%), 255 (M − OC_2H_5, 7), 226 (56), 209 (14), 197 (5), 182 (56), 154 (acenaphthene$^{+\bullet}$, 23), 153 (100), 152 (acenaphthylene$^{+\bullet}$, 44), 141 ($ArCH_2^{+\bullet}$, 80) and 115 (12).

1-Naphthylmethylmalonamide **14**.—A solution of diethyl 1-naphthylmethylmalonate (**13**) (1.00 g, 3.33 mmol) in methanol (3 cm^3) was added to a saturated solution of ammonia in methanol (6 cm^3) containing sodium (6 mg, 0.3 mmol). A precipitate gradually accumulated and was filtered off after 3 days to give white crystals of the title compound **14** (790 mg, 98%), m.p. 262–263 °C (decomp., lit.,[13] m.p. 267–269 °C); δ_H[$(CD_3)_2SO$] 3.46 (2 H, br s, $ArCH_2CH$), 7.09 (2 H, br s, NH), 7.28 (2 H, br s, NH), 7.38 (2 H, m, Ar-H), 7.55 (2 H, m, Ar-H), 7.78 (1 H, d, *J* 6.9, Ar-H), 7.92 (1 H, m, Ar-H) and 8.07 (1 H, d, *J* 7.8, Ar-H); *m/z* 242 (M^+, 42%), 224 (8), 198 (M − $CONH_2$, 75), 181 (65), 154 (acenaphthene$^{+\bullet}$, 22), 153 (55), 152 (acenaphthylene$^{+\bullet}$, 27), 141 ($ArCH_2^{+\bullet}$, 100) and 115 (25).

1-Naphthylmethylmalonitrile **15**.—An intimate mixture of 1-naphthylmethylmalonamide (**14**) (1.00 g, 4.13 mmol) and phosphorus pentaoxide (1.30 g, 9.16 mmol) was heated in a Kugelrohr apparatus at 200 °C at 0.5 Torr. The amber coloured oil which slowly distilled from the dark brown reaction mixture solidified to an oily yellow solid on cooling, to yield 610 mg (72%) of the title compound **15**, which was used immediately without further purification; δ_H(200 MHz; $CDCl_3$) 3.80 (2 H, d, *J* 7.7, $ArCH_2CH$), 4.07 (1 H, dd, *J* 7.1 and 8.1, $ArCH_2CH$), 7.45–7.63 (4 H, m, Ar-H) and 7.81–7.96 (3 H, m, Ar-H); *m/z* 206 (M^+, 20%), 141 ($ArCH_2^{+\bullet}$, 100) and 115 (15).

5-(1-Naphthylmethyl)pyrimidine-2,4,6-triamine **12**.—A solution of sodium ethoxide was prepared from sodium (220 mg, 9.6 mmol) and absolute ethanol (10 cm^3). Guanidinium hydrochloride (600 mg, 6.3 mmol) and 1-naphthylmethylmalononitrile (**15**) (1.18 g, 5.72 mmol) was added and the mixture was refluxed for 3 h, cooled to room temperature and filtered. The filter cake was washed with ethanol (× 1) and water (× 3) and dried, to give the title compound **12** (830 mg, 55%) as a sparingly soluble beige powder, m.p. 276–277 °C (decomp., from $CHCl_3$); δ_H(200 MHz; $CDCl_3$) 4.08 (2 H, s, $ArCH_2$), 4.33 (4 H, br s, 4-NH_2 and 6-NH_2), 4.49 (2 H, br s, 2-NH_2), 7.21 (1 H, dt, *J* 1.1 and 7.1 Hz, Ar-H), 7.37 (1 H, t, *J* 7.7 Hz, Ar-H), 7.56 (2 H, m, Ar-H), 7.76 (1 H, d, *J* 8.3, Ar-H), 7.90 (1 H, dd, *J* 2.4 and 7.0, Ar-H) and 8.12 (1 H, d, *J* 7.5, Ar-H); *m/z* 265 (M^+, 100%) and 138 (pyrimidine-triamine-$CH_2^{+\bullet}$, 14).*

X-Ray Experimental Section.—Suitable single crystals of **5** and **12** were obtained as described above. For each compound one single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. Systematic searches in reciprocal spaces using a Philips PW1100/16 automatic

* *N.B.* Compounds **5**, **6** and **12**, although pure by NMR spectroscopy, did not give satisfactory elemental analyses. In the case of **6**, it has been reported[14] that 5,5-dialkyl-2-aminopyrimidine-4,6-diones burn with great difficulty and even then not without first being mixed with an oxidizing agent. Compound **5** is similar in its physical properties to compound **6**, and, like **12**, its identity is irrefutably established by the X-ray structure.

Table 1 X-Ray experimental data

	5	**12**
Formula	$C_{18}H_{36}N_6O_3$	$C_{19}H_{27}N_5O_2S_2$
Molecular weight	384.5	421.6
Colour	Colourless	
Crystal system	Triclinic	Monoclinic
a/Å	10.089(3)	21.480(6)
b/Å	11.892(3)	12.495(3)
c/Å	9.682(3)	20.486(6)
α/°	95.22(2)	
β/°	101.38(2)	128.18(2)
γ/°	102.76(2)	
V/Å^3	1099.6	4322.1
Z	2	8
D_{calc}/g cm^{-3}	1.161	1.296
λ/Å	1.5418	
μ/cm^{-1}	6.209	23.853
Space group	$P-1$	$C2/c$
Diffractometer	Philips PW1100/16	
Crystal dim. (mm)	0.18 × 0.28 × 0.32	0.12 × 0.23 × 0.32
T/°C	−100	
Radiation	Cu-Kα graphite monochromated	
Mode	$\theta/2\theta$ flying step-scan	
Scan speed (° s^{-1})	0.024	0.020
Step width (°)	0.05	
Scan width (°)	0.90 + 0.14*tg(θ)	
Octants	$\pm h \pm k + l$	$\pm h + k + l$
$\theta_{min/max}$/°	3/54	3/44
Number of data collected	2659	1718
Number of data with $I > 3\sigma(I)$	2242	1188
$A_{min/max}$		0.54/1.08
R(F)	0.056	0.057
R_w(F)	0.086	0.084
p	0.08	0.08
GOF	1.589	1.746

Table 2 Positional parameters and their e.s.d.s for compound **5**

Atom	x	y	z
N(1)	0.569 3(2)	0.431 4(4)	−0.018 4(2)
N(2)	0.663 6(2)	0.334 9(4)	−0.020 7(2)
N(3)	0.627 5(2)	0.508 6(4)	−0.071 1(2)
N(4)	0.705 3(2)	0.164 9(4)	0.035 1(2)
N(5)	0.506 0(2)	0.355 9(4)	0.030 3(3)
C(1)	0.620 2(2)	0.421 2(5)	−0.035 6(3)
C(2)	0.560 5(3)	0.344 5(4)	0.015 8(3)
C(3)	0.656 5(3)	0.250 0(5)	0.016 2(3)
C(4)	0.602 7(2)	0.250 2(4)	0.033 6(3)
C(5)	0.592 6(3)	0.151 6(5)	0.067 8(3)
C(6)	0.651 0(3)	0.136 1(5)	0.161 4(3)
C(7)	0.710 9(3)	0.206 4(5)	0.212 3(3)
C(8)	0.765 4(3)	0.192 5(6)	0.297 8(3)
C(9)	0.759 2(3)	0.107 5(6)	0.334 2(3)
C(10)	0.697 9(3)	0.029 7(5)	0.285 7(3)
C(11)	0.644 7(3)	0.044 4(5)	0.198 7(3)
C(12)	0.585 8(3)	−0.034 6(5)	0.151 2(3)
C(13)	0.577 3(4)	−0.119 8(6)	0.187 1(4)
C(14)	0.629 5(3)	−0.131 4(6)	0.274 4(4)
C(15)	0.688 7(3)	−0.060 2(5)	0.321 7(3)
S(1)	0.830 36(7)	0.042 6(1)	0.725 53(8)
O(1)	0.776 4(2)	0.025 6(3)	0.633 3(2)
C(16)	0.898 4(4)	−0.067 2(6)	0.769 7(4)
C(17)	0.897 7(3)	0.142 8(6)	0.744 0(4)
S(2)	0.397 5(2)	0.824 9(3)	0.616 2(2)
O(2)	0.433 7(2)	0.740 0(3)	0.597 8(2)
C(18)	0.380 2(6)	0.936 7(7)	0.565 1(5)
C(19)	0.481 2(7)	0.881(1)	0.713 5(6)
S(2′)	0.372 6(2)	0.814 9(4)	0.531 8(2)
C(19′)	0.282 7(8)	0.772(2)	0.509(1)

diffractometer showed that crystals of **5** and **12** belong, respectively, to the triclinic and the monoclinic system.

Table 3 Positional parameters and their e.s.d.s for compound **12**

Atom	x	y	z
O(1)	−0.1135(1)	−0.0638(1)	0.7165(1)
O(2)	0.5563(2)	0.2230(2)	1.2166(2)
O(3)	1.4897(2)	0.6675(1)	1.4377(2)
N(1)	0.0703(2)	0.0440(1)	0.6477(2)
N(2)	0.0717(2)	0.0367(1)	0.8896(2)
N(3)	0.2525(2)	0.1546(2)	0.5727(2)
N(4)	0.2599(2)	0.1336(2)	1.0670(2)
N(5)	0.6956(2)	0.1755(2)	1.4047(2)
N(6)	1.3445(2)	0.4912(2)	1.3475(2)
C(1)	0.0065(2)	0.0038(2)	0.7506(2)
C(2)	0.2003(2)	0.1176(2)	0.6834(2)
C(3)	0.2719(2)	0.1510(2)	0.8243(2)
C(4)	0.2029(2)	0.1072(2)	0.9261(2)
C(5)	0.4167(2)	0.2293(2)	0.8649(2)
C(6)	0.5331(2)	0.1652(2)	0.8778(2)
C(7)	0.6763(2)	0.2480(2)	0.9184(2)
C(8)	0.7958(2)	0.1884(2)	0.9513(2)
C(9)	0.9383(2)	0.2722(2)	0.9884(3)
C(10)	0.9849(2)	0.3221(2)	0.8629(3)
C(11)	1.1272(2)	0.4061(2)	0.8980(3)
C(12)	1.1708(3)	0.4512(3)	0.7702(4)
C(13)	0.5728(3)	0.1762(2)	1.3226(3)
C(14)	0.8237(3)	0.2340(3)	1.3712(3)
C(15)	0.7031(4)	0.1255(3)	1.5362(3)
C(16)	1.3883(3)	0.5901(2)	1.4353(3)
C(17)	1.2235(4)	0.4033(3)	1.3533(4)
C(18)	1.4246(4)	0.4667(3)	1.2432(3)

Quantitative data were obtained at −100 °C achieved using a locally built gas flow device. All experimental parameters used are given in Table 1 and non-hydrogen positional parameters are given in Tables 2 and 3 for compounds **5** and **12**, respectively. The resulting data-sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[15] was used with the exception of a local data reduction program. Three standard reflections measured every hour during the entire data collection periods showed no significant trend. The raw step-scans were converted into intensities using the Lehmann–Larsen method[16] and then corrected for Lorentz and polarization factors.

The structures were solved using SIR.[17] In compound **12**, the S and one of the C atoms of the second dimethyl sulfoxide molecule are disordered over two positions in the ratio 1:1 (relative heights in a difference-Fourier map). After refinement of the heavy atoms, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for CH_2 and CH_3 hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as B(H) = 1.3 Beqv(C) Å^2 but not refined. At this stage, empirical absorption corrections were applied to the data for **12** using the method of Walker and Stuart[18] since face indexation was not possible under the cold gas stream. Full least-squares refinements, $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come, respectively, from refs. 19(*a*) and 19(*b*).

Supplementary Material.—For compounds **5** and **12**, respectively: Figs. 7 and 8 with the atom numbering scheme; Tables S1 and S7: isotopic thermal parameters; Tables S2 and S8: temperature factors for anisotropic atoms; Tables S3 and S9: hydrogen-atom positional parameters; Tables S4 and S10: complete set of bond distances; Tables S5 and S11: complete set of bond angles have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme see 'Instructions for Authors (1992),' *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

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