SYMMETRICAL TRIS(4,6-DIAMINO-5-METHYLENE-2-PYRIMIDONES): NEW BUILDING BLOCKS FOR SELF-ASSEMBLY OF HOLLOW SPHERICAL SUPRAMOLECULES LOCKED BY HYDROGEN BONDS

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Dedicated to the memory of Dr Zdenek Arnold.

Concise synthesis of the tris(pyrimidones) **1a,b** is described. Molecular modeling study demonstrated that both the prepared models **1a,b** are capable of self-assembling under formation of spherical dimers locked by 18 hydrogen bonds. Extreme insolubility in all common solvents precluded investigation of the self-assembly in solution. Circumstantial evidence in favor of the self-assembly has been provided in the solid and gas phase.

Key words: Pyrimidones; Hydrogen bonding; Self-assembly.

The spontaneous generation of organized non-covalent structures by self-assembly of complementary molecular units is a leitmotif of supramolecular chemistry. The self-assembling process is driven by molecular recognition between the individual components. Recently, a simple concept has been proposed for the self-assembly which is based on multiple hydrogen bonding[1]. Derivatives of 4,6-diamino-2-pyrimidone[2,3] have been found to be very convenient models for self-assembly by intermolecular hydrogen bonding, each pyrimidone unit providing two self-complementary binding faces. Formation of a highly organized two-dimensional polymeric architecture (Scheme 1) has been demonstrated by X-ray structural analysis[2,3].

Now we wish to extend application of the pyrimidone synthon to construction of closed-surface three-dimensional structures**. Symmetrical tris(pyrimidones) **1** have

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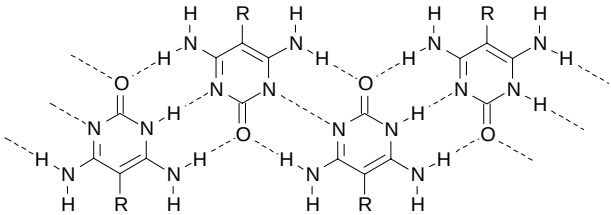
** Successful synthesis of similar self-assembling dimeric capsules based on glycouril or calixarene hydrogen-bonding synthon has been recently reported, see ref.[4].

been designed to serve as the building blocks. According to model examination, their self-assembly might give rise to spherical dimers with a hollow interior locked by six triplets of hydrogen bonds.



SCHEME 1

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. ^{1}H NMR spectra were measured on a spectrometer Varian XL-200 (200 MHz, FT mode) and chemical shifts of protons (δ, ppm) were referred to TMS as the internal standard. Mass spectra (*m/z*, rel.% intensity) were obtained with a ZAB-EQ spectrometer (VG Analytical, Manchester, U.K.); EI mass spectra were taken at 70 eV; matrix and solvent used for FAB spectra are specified in brackets. IR spectra were recorded in KBr pellets and fluorolube mull (4 000–1 350 cm^{-1}) on a Bruker IFS 88 Fourier transform spectrometer. GLC analyses were run on a chromatograph Hewlett–Packard 5890 with a HP-1 column (methylsilicone, 5 m × 0.53 mm, film thickness 2.65 nm); flame ionization detector. TLC analyses were performed on silica gel plates Silufol UV (Kavalier, Votice, Czech Republic).

1,3,5-Benzenetricarbaldehyde (**3a**)

Sodium (8.4 g, 0.37 mol) was dissolved in absolute ethanol (600 ml), 2-nitropropane (52 g, 0.58 mol) was slowly added under intense stirring and the solution was treated immediately with tribromide **2a** (35.7 g, 0.1 mol) dissolved in dimethyl sulfoxide (600 ml). After continuous stirring at room temperature for 3 h the reaction mixture was poured into ice water (3 l) and extracted with chloroform (4 × 300 ml). The combined organic extracts were treated with 3% aqueous sodium hydroxide (350 ml) and washed successively with dilute (1 : 10) hydrochloric acid (270 ml) and saturated aqueous sodium hydrogen carbonate solution (200 ml). After drying ($MgSO_4$) the solution was taken to dryness, the residue was washed with ether and recrystallized from water. Yield 8.4 g (52%), m.p. 158–160 °C, ref.[5] 156.5 °C, ref.[6] 155 °C, ref.[7] 155–159 °C. ^{1}H NMR spectrum was in accord with ref.[7].

2,4,6-Trimethyl-1,3,5-benzenetricarbaldehyde (**3b**)

Prepared analogously from tribromide **2b** (40 g, 0.1 mol). Recrystallization from 2-propanol afforded the pure product (12.5 g, 61%), m.p. 173–260 °C (decomp.). For $C_{12}H_{12}O_3$ (204.2) calculated: 70.57% C, 5.92% H; found 70.63% C, 5.93% H. Mass spectrum (EI): 204 (M^+, 100), 189 (20), 147 (90), 133 (40), 105 (30), 91 (80), 77 (50). ^{1}H NMR spectrum ($CDCl_3$): 2.65 s, 9 H (3 × CH_3); 10.63 s, 3 H (3 × CH=O). IR spectrum ($CHCl_3$): 2 855 w, 2 754 w (CH in CH=O); 1 696 vs (C=O); 1 382 m, 1 071 m (CH_3).

1,3,5-Tris(2′,2′-ethenyldicarbonitrile)benzene (**4a**)

Trialdehyde **3a** (4.86 g, 0.03 mol) was suspended under stirring in 1-butanol (120 ml) and malononitrile (7.27 g, 0.11 mol), followed by several drops of piperidine catalyst (10% solution of the amine in 1-butanol), was added. The reaction mixture was stirred at 50 °C for 8 h, the resulting precipitate was collected by suction, washed successively with water–acetic acid (20 : 1) and ether, and dried in vacuo. Yield 8.90 g (87%), m.p. 288–290 °C (ethyl acetate). For $C_{18}H_6N_6$ (306.3) calculated: 70.59% C, 1.97% H, 27.44% N; found: 70.48% C, 2.01% H, 27.32% N. Mass spectrum (EI): 306 (M^+, 100), 279 (60), 257 (42), 252 (32), 243 (28), 124 (28), 100 (48), 87 (42), 75 (70), 51 (48), 43 (70). ^{1}H NMR spectrum ($(CD_3)_2SO$): 8.48 s, 3 H (3 × CH); 8.78 s, 3 H (Ar-H). IR spectrum (KBr): 3 084 m (CH arom); 3 037 m (HC=C=); 2 237 vs (CN); 1 603 vs (C=C); 1 581 s, 1446 s (ring); 1 192 s, 960 s, 672 s (arom).

1,3,5-Tris(2′,2′-ethenyldicarbonitrile)-2,4,6-trimethylbenzene (**4b**)

Prepared analogously from trialdehyde **3b** (2.04 g (0.01 mol). Yield 2.95 g (85%), m.p. 214–215 °C (1-butanol). For $C_{21}H_{12}N_6$. 0.5 H_2O (357.4) calculated: 70.58% C, 3.67% H, 23.52% N; found: 70.68% C, 3.53% H, 23.71% N. Mass spectrum (EI): 348 (M^+, 100), 333 (18), 320 (30), 306 (42), 279 (32), 267 (15), 140 (15), 120 (22), 100 (15), 88 (20), 76 (15), 63 (20), 57 (20), 51 (18), 39 (20). ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.24 s, 9 H (3 × CH_3); 8.87 s, 3 H (3 × CH). IR spectrum (CH_2Cl_2): 3 024 m (–CH=); 2 962 w, 2 929 w (CH_3); 2 239 s (CN); 1 599 vs (C=C); 1 556 m (ring); 1 450 m (CH_3); 1 383 m (CH_3).

1,3,5-Tris(2′,2′-ethyldicarbonitrile)benzene (**5a**)

Hexanitrile **4a** (2.02 g, 6.6 mmol) was dissolved in dimethylformamide (40 ml) and treated with triethylammonium formate (5.03 g; prepared by a co-distillation of 2 mole equivalents of triethylamine with 5 mole equivalents of formic acid). The reaction mixture was stirred at 25–30 °C for 3 h and poured into ice water (120 ml). The resulting precipitate was collected by suction and washed successively with water and ether. Yield 1.98 g (96%), m.p. 190–192 °C. Mass spectrum (EI): 312 (M^+, 10), 289 (100), 247 (100), 182 (20), 155 (10), 115 (20), 91 (12), 77 (10). HRMS (EI): found 312.1114 (M^+), $C_{18}H_{12}N_6$ requires 312.1123. ^{1}H NMR spectrum ($(CD_3)_2SO$): 3.36 d, J = 7.02 Hz, 6 H (3 × CH_2); 5.07 t, J = 7.02 Hz, 3 H (3 × CH); 7.37 s, 3 H (Ar-H). IR spectrum (KBr): 3 029 w, 3 017 w (CH arom); 2 926 vs, 2 922 vs (CH_2); 2 260 m, 1 607 m (CN); 894 m, 886 m, 723 s.

1,3,5-Tris(2,2′-ethyldicarbonitrile)-2,4,6-trimethylbenzene (**5b**)

Prepared analogously from the hexanitrile **4b** (2.30 g, 6.6 mmol). Yield 2.26 g (97%), m.p. 198–200 °C (acetonitrile). Mass spectrum (EI): 354 (M^+, 20), 289 (100), 262 (10), 224 (35), 159 (42), 128 (35), 115 (20), 91 (18), 69 (30), 55 (38), 43 (40). HRMS (EI): found 354.1544 (M^+), $C_{21}H_{18}N_6$ requires 354.1593. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.41 s, 9 H (3 × CH_3); 3.56 d, J = 8.24 Hz, 6 H (3 × CH_2); 4.87 t, J = 8.24 Hz, 3 H (3 × CH). IR spectrum (KBr): 2 921 s (CH_2); 2 258 m (CN); 1 568 m (ring); 1 479 m, 1 452 m, 1 421 m, 1 365 s (CH_3).

1,3,5-Tris[4′,6′-diamino-5′-methylenepyrimidine-2′(1′*H*)-thione]benzene (**6a**)

To a solution of sodium ethoxide (from 0.3 g, 13.2 mmol of sodium) in ethanol (14 ml) was added thiourea (1.37 g, 18 mmol) and hexanitrile **5a** (1.25 g, 4 mmol). The reaction mixture was heated under reflux for 10 h, and taken to dryness in vacuo. The residue was dissolved in water (15 ml) and neutralized (to pH 6) with dilute hydrochloric acid (1 : 10). The precipitate was collected by suction,

washed successively with water, ethanol and ether, and dried in vacuo. Yield 2.12 g (98%), m.p. >380 °C. Mass spectrum (FAB, thioglycerine + glycerine, DMSO): 541 ([M + H]$^+$, 48), 512 (100), 488 (33), 465 (48), 400 (13), 257 (51). HRMS (FAB): found 541.1396 ([M + H]$^+$), $C_{21}H_{25}N_{12}S_3$ requires 541.1487. ^{1}H NMR spectrum ($(CD_3)_2SO$): 3.68 s, 6 H (3 × CH_2); 6.94 s, 3 H (Ar-H); 7.74 s, 12 H (6 × NH_2); 12.85 brs, 3 H (3 × NH). IR spectrum (KBr): 3 304 vs (NH_2); 3 163 vs (NH); 1 637 vs, 1 567 vs, 1 234 vs, 1 166 s (pyrimidinethione); 1 462 m (benzene); 1 430 m (CH_2); 1 374 (C–N).

1,3,5-Tris[4′,6′-diamino-5′-methylenepyrimidine-2′(1′*H*)-thione]-2,4,6-trimethylbenzene (**6b**)

Prepared analogously from hexanitrile **5b** (1.42 g, 4 mmol). Yield 2.24 g (96%), m.p. >380 °C. Mass spectrum (FAB, thioglycerine + glycerine, DMSO): 583 ([M + H$^+$], 100), 554 (44), 515 (40), 507 (22). HRMS (FAB): found 583.1947 ([M + H$^+$]), $C_{24}H_{31}N_{12}S_3$ requires 583.1957. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.18 s, 9 H (3 × CH_3); 3.71 s, 6 H (3 × CH_2); 6.83 brs, 12 H (3 × NH_2); 12.70 brs, 3 H (3 × NH). IR spectrum (KBr): 3 305 s (NH_2); 3 179 s (NH); 1 626 vs, 1 561 vs, 1 507 vs, 1 227 s, 1 169 s, 964 m (pyrimidinethione); 1 378 s, 1 327 s, 1 299 (C–N).

1,3,5-Tris[4′,6′-diamino-5′-methylenepyrimidine-2′(1′*H*)-one]benzene (**1a**)

Tris(thiopyrimidone) **6a** (540 mg, 1 mmol) was suspended in water (11.2 ml) and heated with chloroacetic acid (0.75 g, 7.94 mmol) under reflux for 3 h. The reaction mixture was then treated with concentrated sulfuric acid (1.35 ml) and heated for another 2 h. The clear solution was neutralized with 30% aqueous sodium hydroxide (to pH 8). The precipitate was collected by centrifugation and washed successively with water and ethanol. Yield 360 mg (73%), m.p. >380 °C. Mass spectrum (FAB, 2-hydroxyethyl disulfide, DMSO): 1 008 ([2 M + Na]$^+$, 2), 985 ([2 M + H]$^+$, 3), 515 ([M + Na]$^+$, 100), 493 ([M + H]$^+$, 95), 401 (80), 369 (25), 279 (80), 237 (100). HRMS (FAB): found 493.2059 ([M + H]$^+$), $C_{21}H_{25}N_{12}O_3$ requires 493.2173. ^{1}H NMR (CD_3COOD + D_2O): 3.72 s, 6 H (3 × CH_2); 7.03 s, 3 H (Ar-H).

1,3,5-Tris[4′,6′-diamino-5′-methylenepyrimidine-2′(1′*H*)-one]-2,4,6-trimethylbenzene (**1b**)

Prepared analogously from tris(thiopyrimidone) **6b** (582 mg, 1 mmol). Yield 450 mg (85%), m.p. >380 °C. Mass spectrum (FAB, 2-hydroxyethyl disulfide, DMSO): 1 091 ([2 M + Na]$^+$, 1), 1 069 ([2 M + H]$^+$, 1), 558 ([M + Na]$^+$, 48), 536 ([M + H]$^+$, 100), 516 (40), 482 (41), 437 (54), 401 (30), 293 (100), 279 (62), 237 (62). HRMS (FAB): found 535.2557 ([M + H]$^+$), $C_{24}H_{31}N_{12}O_3$ requires 535.2642. ^{1}H NMR spectrum (CD_3COOD + D_2O): 2.37 s, 9 H (3 × CH_3); 3.86 s, 6 H (3 × CH_2).

4,6-Diamino-5-benzylpyrimidine-2(1*H*)-thione (**7**)

Prepared from benzylmalononitrile[8] (3.12 g, 20 mmol) by an analogous procedure as **6a**. Yield 4.18 g (90%), m.p. 276–279 °C (dimethylformamide–benzene). Mass spectrum (EI): 232 (M$^+$, 100), 214 (20), 174 (18), 155 (15), 142 (50), 115 (85), 91 (28), 55 (50), 43 (60). HRMS (EI): found 232.0726 (M$^+$), $C_{11}H_{12}N_4S$ requires 232.0783. ^{1}H NMR spectrum ($(CD_3)_2SO$): 3.76 s, 2 H (CH_2); 7.25 m, 5 H (Ar-H); 7.74 brs, 4 H (2 × NH_2); 12.93 brs, 1 H (NH). IR spectrum (KBr): 3 485 s, 3 424 s, 3 269 (NH_2); 3 093 vs (NH); 1 627 vs, 1 572 vs, 1 520 vs, 1 236 vs, 1 176 s, 967 m (pyrimidinethione); 1 495 s, 1 453 m, 1 072 m, 1 030 m, 697 m (benzene); 1 383 s, 1 324 s (CN); 1 196 m (C=S).

4,6-Diamino-5-benzylpyrimidine-2(1*H*)-one (**8**)

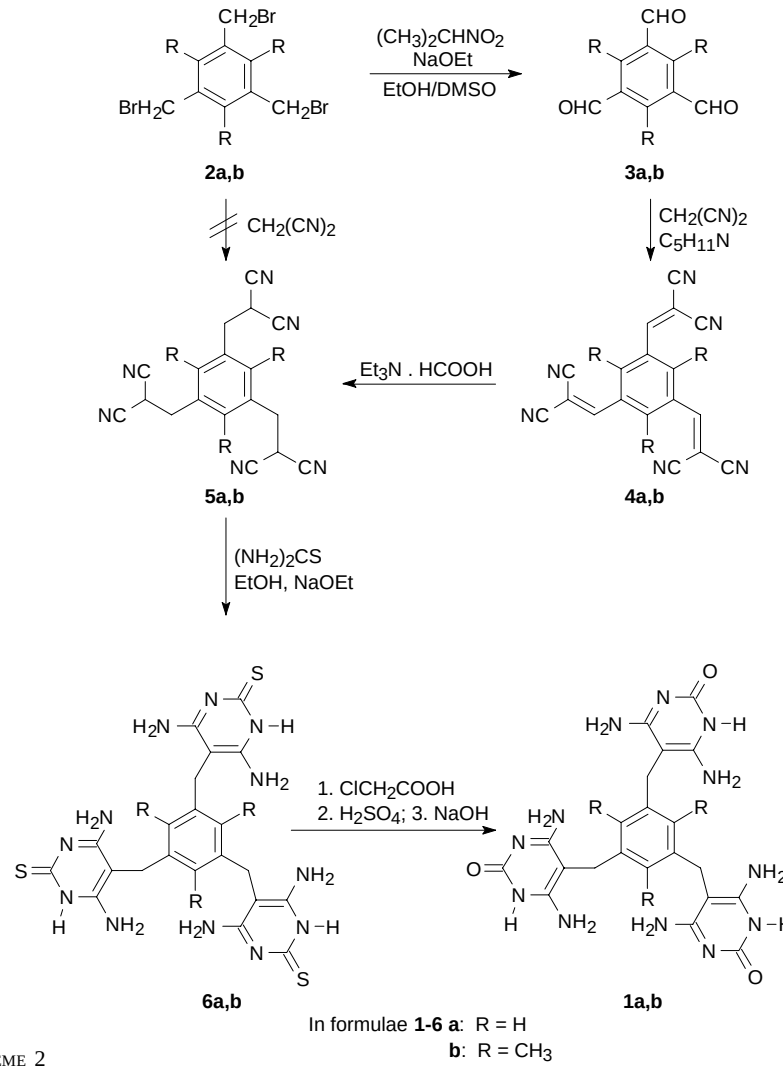
Prepared from **7** (4.18 g, 18 mmol) analogously as described for **1a**. Yield 3.46 g (89%), m.p. 371–374 °C after crystallization from dimethyl sulfoxide. Mass spectrum (EI): 216 (M$^+$, 100), 187 (15), 155 (20),

139 (22), 122 (15), 91 (15), 69 (20), 57 (32), 43 (30). HRMS (EI): found 216.1003 (M^+), $C_{11}H_{12}N_4O$ requires 216.1011. ^{1}H NMR spectrum (D_2O + CD_3COOD): 3.76 s, 2 H (CH_2); 7.34 m, 5 H (Ar-H).

RESULTS AND DISCUSSION

Synthesis

The synthetic protocol used for the preparation of the target tris(4,6-diamino-5-methylene-2-pyrimidones) **1a,b** is outlined in Scheme 2.



SCHEME 2

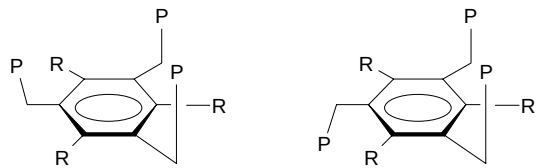
The starting tribromides **2a,b** have been prepared from mesitylene, the former by radical bromination[9] and the latter by bromomethylation[10]. Since the direct alkylation of malononitrile with the tribromides **2a,b** failed to afford the corresponding tris(malononitriles) **5a,b**, an alternative procedure had to be developed. Tribromides **2a,b** have been accordingly converted into the trialdehydes* **3a,b** upon a treatment with 2-nitropropane carbanion[13] in EtOH–DMSO solution. Knoevenagel condensation[14] of the trialdehydes **3a,b** with malononitrile afforded smoothly the unsaturated hexanitriles **4a,b**. Triethylammonium formate has been found to be a mild and highly selective reducing agent[15] for conversion of **4a,b** into the desired saturated analogues **5a,b**. Condensation of **5a,b** with thiourea afforded tris(thiopyrimidones) **6a,b** which upon treatment with chloroacetic acid and subsequent hydrolysis yielded the target building blocks **1a,b.**

Analogous protocol, starting from benzaldehyde, was used for the preparation of 4,6-diamino-5-benzyl-2-pyrimidone **8** serving as a reference compound.

Molecular Modeling Studies

The structures of tris(pyrimidones) **1a,b** have been optimized at the semiempirical PM3 level[16] using program package MOPAC[17]. The calculation shows that the derivative **1a** (R = H) should exist preferably in a "cone" conformation that is by ≈20 kJ/mol more stable than the alternative "alternate" arrangement.

Further examination of the optimized conformation of **1a** shows that interpenetration



"cone" "alternate"

P = 2,4-diaminopyrimidine-2-(1*H*)-thion-5-yl; R = H, CH_3

of two head-to-head oriented "cones", twisted mutually by 60°, allows formation of interleaved supramolecular dimer that seals the resulting cavity by intermolecular hydrogen bonds. The symmetry of the dimer can be seen from a top view (Fig.1a), whereas the hydrogen bonding network among the individual pyrimidone units, which totals 18 hydrogen bonds, is apparent from the side view (Fig. 1b). Based on the dif-

* Several other synthetic approaches have been earlier reported for preparation of **3a**, cf. e.g. refs[5–7]. Two ingenious syntheses have been designed by the late Dr Z. Arnold (refs[11,12]).

ference between energies of the optimized dimer and monomer, the energy gain resulting from the non-covalent dimerization corresponds to about 158 kJ/mol.

In a contrast, the corresponding energy gain calculated for the analogous dimerization of the tris(pyrimidone) **1b** (R = CH_3) amounts only to ≈70 kJ/mol. A steric interference between the individual pyrimidone units and the neighboring methyls is assumedly responsible for this difference between **1a** and **1b**. Notably, molecular modeling studies show that the "cone" conformation of the monomeric form of **1b** is less stable than the "alternate" arrangement, in a contradistinction to the situation found above for the non-methylated compound **1a**.

Observed Self-Assembling Properties

Examination of self-assembling properties of the tris(pyrimidones) **1a,b** is rendered difficult by extreme insolubility of these compounds, the sole exception being strongly acidic solvents (e.g. CF_3COOH) destroying the hydrogen bonding networks. Self-assembling studies in solution could not be accordingly accomplished and acquiring the physico-chemical evidence has been confined to the solid and gas phase.

IR spectra of the pyrimidones **1a,b** and **8** have been taken in KBr pellets as well as in fluorolube mull and the main data are summarized in Table I. The assignment of the individual bands is based on the available spectral analysis of the structurally akin cytosine[18].

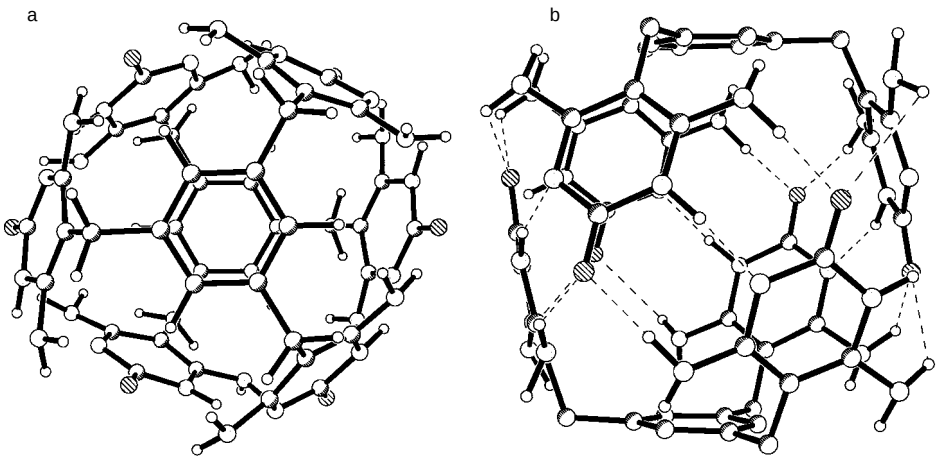


FIG. 1
A top (a) and side (b) view on the optimized structure of the dimer **1a.1a**

All the three investigated pyrimidones exhibit two intense and very broad bands in the region 3 300–3 000 cm^{-1}, the upper corresponding to the antisymmetric valence vibration of the $–NH_2$ groups bound strongly by hydrogen bonds (cytosine 3 380 cm^{-1}), whereas the lower originates assumedly from valence vibration of the N–H bonds, also strongly hydrogen bound (cytosine 3 169 cm^{-1}). At higher wavenumbers the band corresponding to the bound $–NH_2$ groups is complemented by the corresponding band of the "free" (unbound) form. Thus, in accord with expectation, both tris(pyrimidones) **1a,b** as well as the mono(pyrimidone) **8** exhibit qualitatively the same hydrogen bonding pattern in the solid phase.

Relative strength of the hydrogen bonds in the individual models was assessed on the basis of the observed shifts of $\nu(NH_2)$, $\nu(NH)$ and $\beta(NH)$. It is seen from the cursory inspection of the data in Table I that the intermolecular hydrogen bonding is somewhat stronger in the mono(pyrimidone) **8** than in both the tris(pyrimidones) **1a,b**, in a qualitative accord with the non-ideal arrangement of hydrogen bonds anticipated in the spherical dimers of **1a,b**.

TABLE I
Infrared spectra of diaminopyrimidone derivatives **1a,b** and **8** in the region 3 500–950 cm^{-1} (KBr pellets)[a]

Assignment[b]	**1a**	**1b**	**8**
$\nu_{as}(NH_2)$ free	3 462 m	3 439 m[c]	3 483 s; 3 469 s
$\nu_{as}(NH_2)$ bonded	3 350 m	3 329 m[c]	3 321 s
$\nu(NH)$	3 198 m	3 124 m	3 129 vs; 3 026 vs
$\beta_s(NH_2)$	1 678 s, sh	1 678 s, sh	1 680 s, sh
$\nu(C=O)$, ν(ring)	1 627 vs	1 621 vs	1 638 vs
$\beta(NH) + \nu$(ring)	1 559 s	1 552 s	1 569 s
ν(ring) + $\beta(NH)$	1 506 s	1 498 s	1 511 vs
ν_{as}, $\nu_a(C–N)$	1 420 s; 1 374 m	1 412 s; 1 376 m[d]	1 424 vs; 1 396 vs
ν(ring)	1 234 w; 1 141 m	1 242 w, sh; 1 1140 w	1 237 m; 1 156 m; 1 141 m
ν(ring) + $\beta_{as}(NH_2)$	1 070 w, sh	1 070 w, sh	1 076 m[e]
ν, β(ring)	997 w	995 w	1 001 m

[a] Benzene, CH_2 and CH_3 vibrations and many shoulders on broad, complex bands are omitted; vs very strong, s strong, m medium, w weak, sh shoulder. [b] ν_{as}, ν_s antisymmetric and symmmetric stretching, β in plane bending, β_s scissoring, β_{as} rocking, δ bending. [c] Value from fluorolube mull spectrum. [d] Overlapping with $\delta_s(CH_3)$. [e] Overlapping with benzene vibration.

There is some indication that the self-assembled dimers **1a.1a** and **1b.1b** may occur also in the gas phase. The FAB spectra of both tris(pyrimidones) **1a** and **1b** showed the presence of small but significant peaks $[2\ M + H]^+$ and $[2\ M + Na]^+$.

Summing up, several pieces of circumstantial but not yet conclusive evidence have been provided supporting feasibility of the projected spherical dimers. Studies aiming at preparation of more soluble (lipophilic) analogues are in progress.

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