$a=b=16.387(2)$, $c=8.279(1)$ Å, $Z=6$, $V=1925$ Å^3, $\rho_{calcd}=1.548\,\mathrm{g\,cm^{-3}}$, white powder, $\lambda=1.5406$ Å, T≈25°C, data range 5–100° (2θ), 1900 data points, 30 independent reflections, no absorption correction, Rietveld refinement with X-ray powder data with geometrical constraints; data range used 9–70° (2θ), $R_p=16.7$, $R_{wp}=18.0$, $R_B=8.6$, $\chi^2=3.5$, $R_p=100\Sigma|y_{oi}-y_{ci}|/\Sigma|y_{oi}|$, $R_{wp}=100(\Sigma w|y_{oi}-y_{ci}|^2/\Sigma w|y_{oi}|^2)^{0.5}$, $R_B=100\Sigma|I_k-I_{ck}|/\Sigma|I_k|^2=(R_{wp}/R_{exp})^2$. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshaften (Germany), on quoting the depository number CSD-407150.

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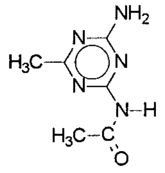
Self-Complementarity Achieved through Quadruple Hydrogen Bonding**

Felix H. Beijer, Huub Kooijman, Anthony L. Spek, Rint P. Sijbesma, and E. W. Meijer*

Hydrogen bonds are among the most useful interactions for encouraging molecules to self-assemble into well-defined aggregates.[1] The strength and selectivity of hydrogen bonds can be increased by introducing arrays of donor (D) and acceptor sites (A). Arrays of two and three hydrogen bonds have already been studied in detail, and their strength in $CHCl_3$ depends upon the particular arrangement of donor and acceptor sites. In triply hydrogen bonded complexes, for example, association constants vary from $K_a=10^2-10^3\,\mathrm{M^{-1}}$ for DAD–ADA pairs to $K_a=10^5-10^6\,\mathrm{M^{-1}}$ for DDD–AAA pairs.[2] Jorgensen[3] rationalized these differences as the result of secondary electrostatic interactions. Rules derived from this analysis are now widely used to design complementary host–guest systems characterized by high selectivity and recognition as well as strong binding.

However, for a number of applications ranging from container molecules[4] to supramolecular tubes,[5] self-complementarity is required. This is evidently found only in arrays with an even number of hydrogen bonds. Although examples exist of self-complementary arrays consisting of two hydrogen-bonding units,[6] arrays with four adjacent hydrogen-bonding sites are notably absent from the supramolecular literature.[7] Recently we reported the dimerization of a diacetyl diaminotriazine involving four hydrogen bonds with a dimerization constant K_{dim} of $35\,\mathrm{M^{-1}}$.[8]

Here we show the generality of dimerization by way of the DADA sequence in readily available compounds, and present examples with unexpectedly high dimerization constants. Conceptually, the DADA arrays in compounds **1–6** are derived from DAD arrays in diaminotriazines or diaminopyrimidines that have been extended by an oxygen acceptor atom from a *cis* amido or ureido group. The required *cis*-amide conformation in **1**, **2**, and **5** is favored by repulsion between the amide oxygen atom and nitrogen atoms in the heterocyclic ring, whereas an intramolecular hydrogen bond preorganizes the array in ureido derivatives **3**, **4**, and **6**.



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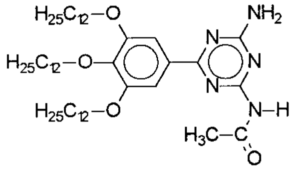

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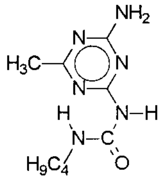

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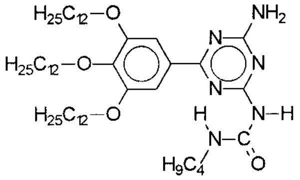

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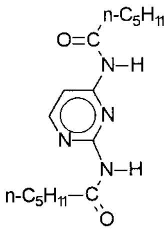

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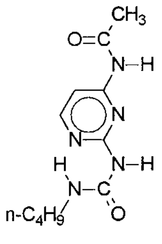

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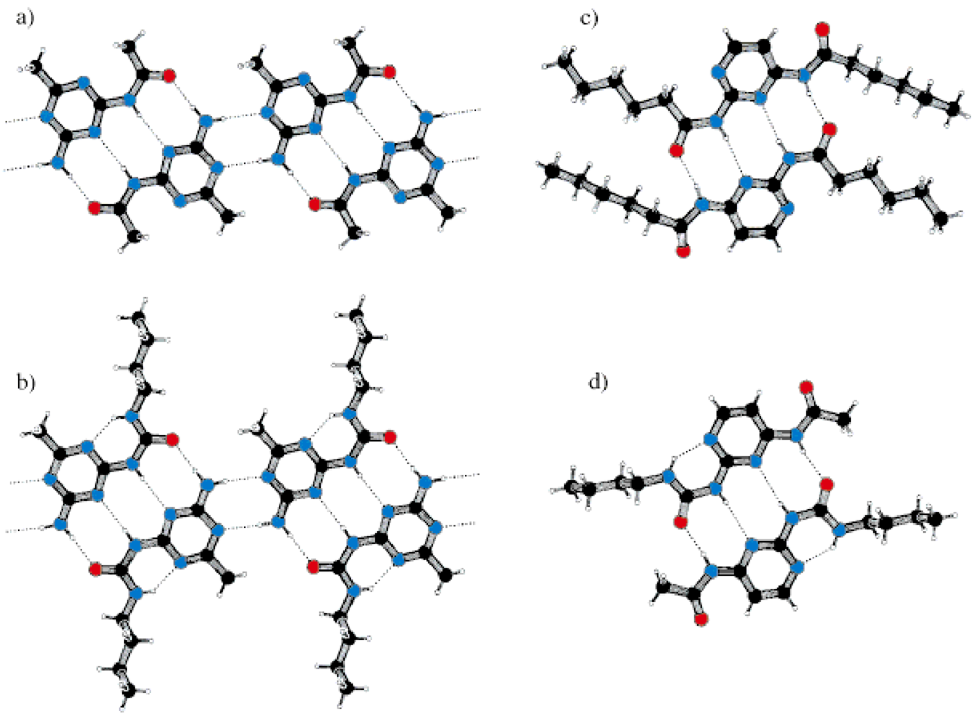

Figure 1. PLUTON representations of the structures of a) **1**, b) **3**, c) **5**, and d) **6**.

Compounds **1**–**6** were prepared by acylation of diaminotriazine and diaminopyrimidine derivatives. The structures of **1**, **3**, **5**, and **6** were determined by single-crystal X-ray diffraction (Figure 1).[9] All four compounds form centrosymmetric dimers in the solid state, which are held together by four hydrogen bonds between self-complementary DADA arrays. The dimers of triazines **1** and **3** form infinite chains by double hydrogen bonding of the remaining N–H group to a triazine-ring nitrogen atom. An additional intramolecular hydrogen bond is present in ureido derivatives **3** and **6** from the ureido nitrogen atom to a ring nitrogen atom. Distances between hydrogen-bonded atoms are listed in Table 1. The DADA arrays in all four crystal structures deviate significantly from linearity. Thus, the oxygen atom does not fall on the line joining the nitrogen atoms in the array. As a result, the inner N–H$\cdots$N hydrogen bonds are 0.30–0.49 Å longer than the outer N–H$\cdots$O hydrogen bonds. Apparently, the enforced differences in bond lengths between N–H$\cdots$O and N–H$\cdots$N hydrogen bonds (which have similar equilibrium lengths)[10] does not prevent the formation of stable dimers.

FT-IR spectra of solid samples and concentrated solutions of **2**, **4**, **5**, and **6** in chloroform are very similar both in the N–H region (3500–3170 cm^{-1}) and in the double-bond region (1750–1400 cm^{-1}), which indicates a similar complexation mode in the solid state and in solution. Dilution of the solutions in chloroform results in the appearance of the monomer IR spectrum. This permits derivation of both monomer and dimer absorptions, as well as the shifts that accompany complexation; all are typical for hydrogen bonding. Changes in the N–H stretching vibrations of **5** and **6** upon dimerization are very similar [$\Delta\nu = 167$ and 235 cm^{-1} (**5**) and 158 and 256 cm^{-1} (**6**)], which indicates that the hydrogen bonds themselves are similar.

^{1}H and ^{13}C NMR spectra taken both in chloroform and DMSO are in agreement only with the tautomeric form indicated in the structural formulas. In the ^{1}H NMR spectra of the soluble compounds **2**, **4**, **5**, and **6** the chemical shifts for the amide protons in chloroform are concentration-dependent. When the concentration is increased, the signals shift downfield, which indicates formation of a hydrogen-bonded complex. The concentration dependence of the N–H shifts can be simulated only with a model that assumes dimerization. Dimerization constants can be obtained from this model for **2**, **4**, and **5** (Table 2). The dimerization constant for **4** was determined to be 2.2×10^{4} M^{-1} by evaluation of IR spectra at

Table 2. Dimerizaton constants for **2** and **4**–**6** in CDCl$_3$ at 298 K.

Compound	K_{dim} [M^{-1}][a]	$-\Delta G_{\text{dim}}$ [kJ mol^{-1}]
2	530	15.5 ± 0.5
4	2×10^{4}[b]	24.5 ± 0.3
5	170	12.7 ± 0.5
6	2×10^{5}	30.2 ± 0.5

[a] Estimated relative error <20%. [b] Average of values determined by IR and NMR spectroscopy.

Table 1. Hydrogen-bond distances [Å] and X-H-X angles [°], differences in length between inner and outer hydrogen bonds, as well as N$\cdots$N$\cdots$O angles in the DADA array.

	NH$\cdots$N distance	NH$\cdots$N angle	NH$\cdots$O distance	NH$\cdots$O angle	Difference in hydrogen-bond length	N$\cdots$N$\cdots$O angle
1	3.195(2)	175(2)	2.839(2)	175(2)	0.3556	169.60(6)
3	3.101(4)	176(3)	2.797(4)	176(3)	0.304	171.0(1)
5	3.245(2)	166(2)	2.789(2)	162(2)	0.456	167.71(7)
6	3.239(4)	171(2)	2.748(3)	169(2)	0.491	167.99(8)

various concentrations, whereas a value of $1.5 \times 10^4\,\mathrm{M}^{-1}$ was obtained from NMR measurements. The dimerization constant of **6** is too high to be determined directly in $CDCl_3$. Limiting shift values for **6** in $CDCl_3$ containing 1, 2, 3, 4, and 5% methanol are identical, so these values can be used for extrapolation to pure $CDCl_3$. This results in an estimate for the dimerization constant in pure $CDCl_3$ of approximately $2 \times 10^5\,\mathrm{M}^{-1}$.

The dimers of **2** and **4**–**6** in chloroform show remarkably different stabilities. Although all the dimers are stabilized by four intermolecular hydrogen bonds, the stabilities differ by as much as $17.5\,\mathrm{kJ\,mol^{-1}}$. The most significant differences are observed between amide derivatives **2** and **5** on one hand, and ureido derivatives **4** and **6** on the other.

Sartorius and Schneider have recently proposed a simple free-energy relationship for the stability of multiply hydrogen bonded complexes in chloroform.[11] This is based on two increments: $7.9\,\mathrm{kJ\,mol^{-1}}$ for each hydrogen bond and $\pm 2.9\,\mathrm{kJ\,mol^{-1}}$ for each attractive or repulsive secondary electrostatic interaction. The increments were derived from association data for heterocyclic compounds with spatially fixed arrays. A dimerization constant of $310\,\mathrm{M}^{-1}$ ($\Delta G^\circ_{\mathrm{dim}} = -14.2\,\mathrm{kJ\,mol^{-1}}$) is predicted for a DADA array. The dimerization constants for amides **2** and **5** ($K_{\mathrm{dim}} = 530$ and $170\,\mathrm{M}^{-1}$, respectively) agree with the predictions, provided one takes into account the considerable degree of rotational freedom available. Most surprisingly, however, ureido derivatives **4** and **6** display stabilities that exceed the calculated values by 10.3 and $16.0\,\mathrm{kJ\,mol^{-1}}$, respectively. The increased stability of the dimers from **4** and **6** relative to the dimers from **2** and **5** might be ascribed to preorganization of the DADA array provided by the intramolecular hydrogen bonds in these compounds, which fix the carbonyl groups in the plane of the ring. In both compounds a *cis* conformation for the amide groups and coplanarity with the aromatic ring are required for dimerization. Fixation of the amide in this conformation is unfavorable not only entropically, but also enthalpically.[12] Therefore, we propose that the higher stability of dimers of the ureido compounds compared to amido derivatives is caused by a combination of favorable entropic and enthalpic effects of the intramolecular hydrogen bonds of the ureido substituents. Although the difference in stability of dimers in the two series can indeed be explained this way, the argument does not account for the large deviations of the values for **4** and **6** from those calculated by Sartorius and Schneider;[11] this requires further investigation.

Self-complementary quadruply hydrogen bonded systems can be prepared very readily by acylation of DAD arrays, and the stabilities of the resulting dimers are anomalously high when the array is preorganized by intramolecular hydrogen bonds. Further elaboration of self-complementarity and preorganization by intramolecular hydrogen bonds, together with the application of four-point recognition in supramolecular chemistry, are the subjects of ongoing research.

Experimental Section

Dimerization studies in chloroform: Dimerization constants (K_{dim}) were obtained through ^{1}H NMR titrations, in which the shift of the N−H protons (as well as aromatic and CH_3 protons, where appropriate) was monitored as a function of concentration. At least ten data points in the 20–80% saturation range were measured, and dimerization constants were evaluated by nonlinear least-squares fitting of the data to the appropriate equation.[13] ^{1}H NMR titrations utilized $CDCl_3$ (Cambridge Isotope Laboratories, 99.8% D content, with TMS as internal reference). For the IR studies, freshly prepared anhydrous chloroform[8] was used.

1-6: Acetylaminotriazines **1** and **2** and ureidotriazines **3** and **4** were synthesized by heating the corresponding diaminotriazine in pyridine at reflux with excess acetic anhydride (15 min)[14] or excess butyl isocyanate (2 h). Cooling resulted in precipitation of pure **1** and **3**, and crystallization from DMF afforded crystals of sufficient quality for single-crystal X-ray analysis. Derivatives **2** and **4** were purified by precipitation in hexane or ethyl acetate and by column chromatography. Di(hexanoylamino)pyrimidine (**5**) was obtained by heating 2,4-diaminopyridine with hexanoic anhydride in pyridine at reflux for 2 h and crystallization from hexane/ethyl acetate. Crystals suitable for single-crystal X-ray analysis were obtained by evaporating a solution in hexane/dichloromethane under air. 2-Butylureido-4-acetylaminopyridine (**6**) was synthesized in two steps. Reaction of 2,4-diaminopyridine in warm THF with 1 equiv of butyl isocyanate afforded, after crystallization, pure 2-butylureido-4-aminopyridine. This was treated with 1 equiv of acetyl chloride in warm THF. Crystals suitable for single-crystal X-ray analysis were obtained by evaporating a solution in dichloromethane under air. All compounds provided satisfactory analyses. Full details regarding synthesis and characterization, together with a study of the observed association behavior, including bis-acylated derivatives, will be published elsewhere.

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flections with $I > 2\sigma(I)$], $S = 1.041$ for 136 parameters. A final difference Fourier map showed no residual density below -0.30 or above $0.28\ e\,Å^{-3}$. Crystal data for **3** $\cdot C_9H_{16}N_6O$: $M_r = 224.27$, colorless needle-shaped crystal ($0.05 \times 0.10 \times 0.50\ mm^3$), triclinic, space group $P\bar{1}$ (no. 2), $a = 4.703(2)$, $b = 7.924(6)$, $c = 15.833(18)$ Å, $\alpha = 78.69(9)$, $\beta = 86.18(6)$, $\gamma = 74.43(6)°$, $V = 557.3(8)\ Å^3$, $Z = 2$, $\rho_{calcd} = 1.3365(19)\ g\,cm^{-3}$, $F(000) = 240$, $\mu(Mo_{K\alpha}) = 0.9\ cm^{-1}$. Data collection and reduction as well as solution and refinement were conducted as described for **1**. Of 4350 measured reflections, 2567 were independent; $R_{int} = 0.059$, ($1.3 < \tau < 27.5$). The refinement converged at $wR_2 = 0.1323$, $w = 1/[\sigma^2(F^2) + (0.0465\,P)^2 + 0.07\,P]$, $R_1 = 0.0553$ [for 1474 reflections with $I > 2\sigma(I)$], $S = 1.021$ for 193 parameters. A final difference Fourier map showed no residual density below -0.22 or above $0.27\ e\,Å^{-3}$. Crystal structure data for **5** $\cdot C_{16}H_{26}N_4O_2$: $M_r = 306.41$, colorless block-shaped crystals ($0.2 \times 0.3 \times 0.5\ mm^3$), triclinic, space group $P\bar{1}$ (no. 2), $a = 4.9675(11)$, $b = 8.1236(7)$, $c = 20.911(3)$ Å, $\alpha = 100.663(9)$, $\beta = 93.080(15)$, $\gamma = 91.680(12)°$, $V = 827.4(2)\ Å^3$, $Z = 2$, $\rho_{calcd} = 1.2299(3)\ g\,cm^{-3}$, $F(000) = 332$, $\mu(Mo_{K\alpha}) = 0.8\ cm^{-1}$. Data collection and reduction as well as solution and refinement were conducted as described for **1**. Of 4552 measured reflections, 3814 were independent, $R_{int} = 0.055$, ($1.0 < \tau < 27.5$). The refinement converged at $wR_2 = 0.1567$, $w = 1/[\sigma^2(F^2) + (0.0880\,P)^2 + 0.31\,P]$, $R_1 = 0.0553$ [for 2963 reflections with $I > 2\sigma(I)$], $S = 1.015$ for 277 parameters. A final difference Fourier map showed no residual density below -0.27 or above $0.34\ e\,Å^{-3}$. Crystal structure data for **6** $\cdot C_{11}H_{17}N_5O_2$: $M_r = 251.29$, colorless needle-shaped crystals ($0.1 \times 0.1 \times 0.7\ mm^3$), monoclinic, space group $C2/c$ (no. 15), $a = 20.119(18)$, $b = 5.194(2)$, $c = 25.186(16)$ Å, $\beta = 94.55(4)°$, $V = 2624(3)\ Å^3$, $Z = 8$, $\rho_{calcd} = 1.2722(15)\ g\,cm^{-3}$, $F(000) = 1072$, $\mu(MoK_\alpha) = 0.9\ cm^{-1}$. Of 8860 measured reflections, 3007 were independent; $R_{int} = 0.075$, ($1.0 < \tau < 27.3$, $T = 293$ K) using an Enraf–Nonius FAST area detector on a rotating anode. Data collection and reduction as well as solution and refinement were conducted as described for **1**. The refinement converged at $wR_2 = 0.1332$, $w = 1/[\sigma^2(F^2) + (0.0300\,P)^2 + 4.33\,P]$, $R_1 = 0.0644$ [for 2305 reflections with $I > 2\sigma(I)$], $S = 1.160$ for 214 parameters. A final difference Fourier map showed no residual density below -0.25 or above $0.25\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100480. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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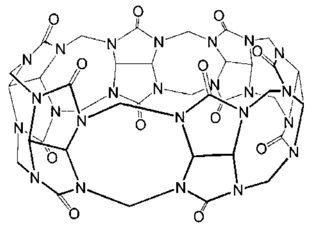
A Molecular Bowl with Metal Ion as Bottom: Reversible Inclusion of Organic Molecules in Cesium Ion Complexed Cucurbituril[**]

Dongmok Whang, Jungseok Heo, Joo Hyun Park, and Kimoon Kim[*]

Molecular containers,[1] rigid molecules with large cavities in which small molecules can be encapsulated, are of much interest because of their potential applications in separations, catalysis, sensors, and drug delivery. Although a number of molecular container systems have been studied only a few of them have demonstrated reversible encapsulation and release of their guests at ambient temperatures.[2, 3] We recently reported[4] a novel molecular container assembly based on cucurbituril (**1**),[5, 6] a macrocyclic cavitand with a hollow core of ≈5.5 Å diameter, which is accessible through two portals laced with carbonyl groups. In aqueous solution containing sodium ions, two Na^+ ions and their coordinated water molecules cover each portal of cucurbituril like a lid on a barrel.[4, 7] The "Na^+-lidded" cucurbituril can encapsulate small organic molecules such as THF and benzene. Moreover, the encapsulation and release of the guest molecules can be controlled by complexation and decomplexation of the sodium ions at the portals. Extending this work to cucurbiturils complexed to other alkali metal ions, we thought cesium-complexed cucurbituril would be particularly interesting because Cs^+, whose ionic radius is 1.81–2.02 Å seems to fit the portal better. Indeed, Cs^+-complexed cucurbiturils are drastically different from the Na^+-complexed cucurbiturils.[4] Here we report the cesium-complexed cucurbiturils, which uniquely behave like a "metal-ion-bottomed" molecular bowl.



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Although cucurbituril is sparingly soluble in water it dissolves appreciably in cesium chloride solution ($\approx 5.9 \times 10^{-2}$ mol in 1.0 L of 0.2 M CsCl solution at room temperature) as it does in aqueous solutions of other alkaline metal salts. Slow diffusion of ethanol into cucurbituril dissolved in 0.2 M CsCl solution results in the formation of crystals of **2**. The X-ray crystal structure of **2** (Figure 1)[8] reveals that a cesium ion is coordinated to each portal of cucurbituril, but the structure is in sharp contrast to the sodium-complexed cucurbituril in which two sodium ions are coordinated to each portal of cucurbituril.[4] The cesium ion leans toward one side of the portal, being coordinated to only four carbonyl oxygen atoms

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