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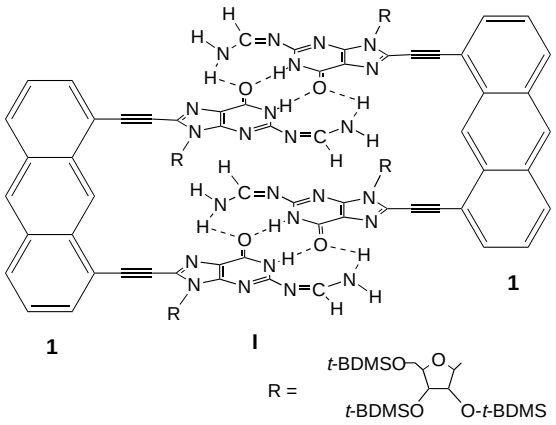
[21] Transition states leading to *trans* ring junctures are not considered based on previous experience.[6b, 9] The alternate chairlike conformation that may lead to **33** is not shown, since it displays severe 1,3-diaxiallike interactions.

A New Base-Pairing Motif Based on Modified Guanosines**

Jonathan L. Sessler* and Ruizheng Wang

Watson – Crick base pairing involving purine and pyrimidine subunits plays a crucial role in regulating the structures and properties of, for example, duplex DNA and hairpin RNA. Studying synthetic systems with unconventional binding modes could serve to extend the genetic alphabet of DNA and RNA, and produce systems of greater structural diversity, functionality, and catalytic potential.[1] In this context, modified systems derived from guanine are of considerable interest because of their potential antiviral activity and their possibly unique binding ability.[2] However, the number of such systems that have been analyzed in terms of their self-association properties remains limited. One example is 7,9-dimethylguanine, a species that dimerizes in aqueous solution with the formation of three hydrogen bonds.[3] A second example is 5′-(*tert*-butyldimethylsilyl)-2′,3′-*O*-isopropylidene isoguanosine; this forms a tetramer[4] in organic media that is more stable than the corresponding guanosine tetramer.[5] Here we report the new guanine derivative **1**, which, when constrained within a rigid framework, self-associates in organic solution to form an unprecedented tetrameric guanine-containing array (dimer **I**). What is unique about this system is that it is held together by a pair of four-point hydrogen bonds.[6–8]



The synthesis of **1** (Scheme 1) involves initially a Pd-catalyzed cross-coupling between N^2-(*N*,*N*-dimethylformamidine)-protected 8-bromoguanosine (**5**) and organostannyl derivative **4**[9] produced in situ from 1,8-diethynylanthracene (**3**). This sequence gave the bis(guanosine) derivative **6**. Treatment of **6** with methanolic ammonia at room temperature did not give the expected deprotected bis(guanine) derivative **2**, but rather **1**, in which the NMe_2 group of **6** is

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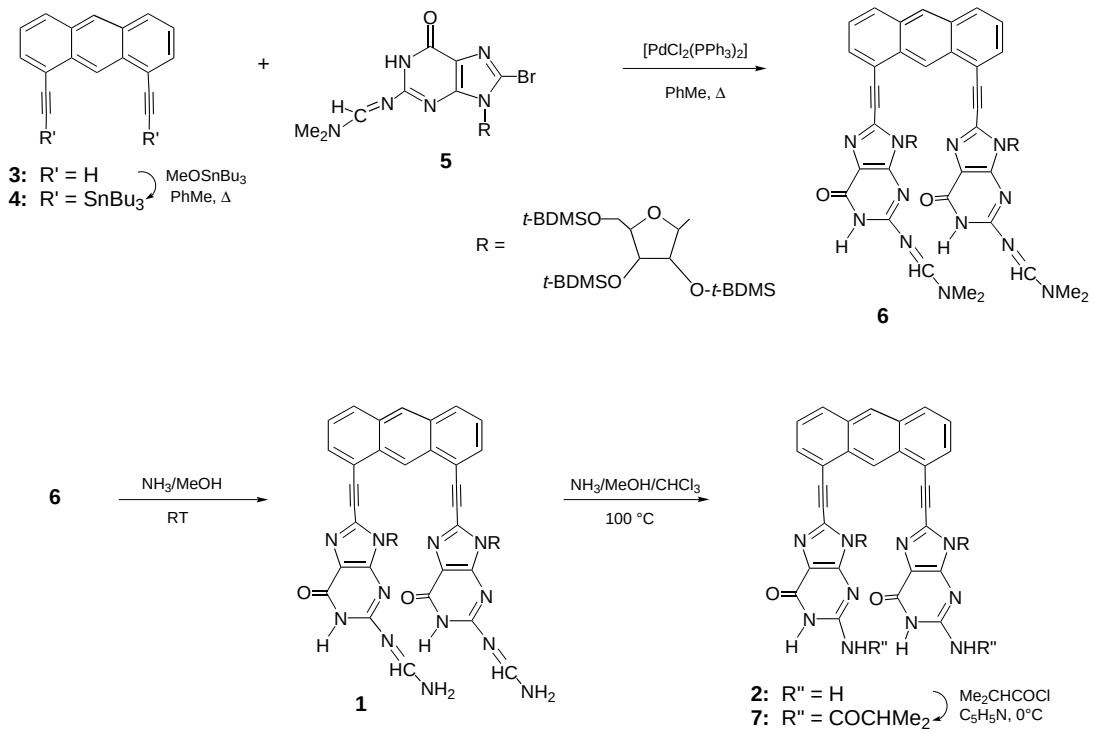

Scheme 1. Synthesis of **1** and **2**.

replaced by an NH_2 group. Compound **2** could then be obtained by treating **1** with methanolic ammonia in chloroform at 100 °C in a sealed tube. The amino groups in **1**, which are "extended" by two bonds with respect to those in **2**, were found to impart unique binding properties. Accordingly, compound **1** was characterized by ^1H and ^{13}C NMR spectroscopy (including $^1H-^1H$ COSY, $^1H-^{15}N$ HMQC, and ^1H-^{13}C HMQC experiments), mass spectrometry, elemental analysis, and a detailed study of its general chemical properties.

Compound **1** is extremely nonpolar. It displays, for instance, an R_f value of 1 (thin-layer chromatography (TLC) on silica gel, hexane/ethyl acetate 3/1) under conditions where **2**, **5**, **6**, and **7** display R_f values close to 0. Derivative **1** is also highly solubile in nonpolar solvent such as benzene and toluene, and insoluble in pure DMSO and acetone. While puzzling at first, the low effective polarity of **1** was in due course rationalized by the self-associated formation of ensemble **I**. In this dimer the functional groups in **1** are tied up in intradimer hydrogen bonds and therefore unavailable for interaction with a polar solvent or solid support.

Initial evidence that **1** can self-associate to form a stable dimer came from fast atom bombardment mass spectrometry (FAB-MS). In addition to a peak at $m/z = 1527$, ascribable to the monomer, a second peak at $m/z = 3054$ was also seen (no peaks ascribable to higher order aggregates were observed). A high-resolution analysis of the latter signal proved consistent with the proposed existence of a dimer (calcd for $C_{152}H_{237}N_{24}O_{20}Si_{12}$: $M_r = 3054.5503$; found: 3054.5492). Such dimer peaks, however, were not seen in the FAB mass spectra of three control compounds, namely, **2**,[10] **6**, and **7**.

The average molecular weight of **I** was measured in solution with vapor pressure osmometry (VPO; 1,2-dichloroethane as the solvent and diphenylacetylene as the standard). The value obtained (3125 ± 190 u; 30 °C) agrees well with that calculated for the proposed dimeric structure **I** (3054 u).

More compelling evidence for the formation of ensemble **I** came from NMR spectroscopic analyses.[11] Simple ^1H NMR studies revealed that the chemical shifts of the imino NH resonances in $CDCl_3$ were at $\delta = 13.6$, 12.6, 10.6, 11.0, and 11.7 for compounds **1**, **2**, **5**, **6**, and **7**, respectively. The large downfield shifts for the imino NH protons in **1** and **2** are consistent with the suggestion that they are involved in hydrogen bonding.[12]

$^1H-^{15}N$ HMQC NMR experiments in C_6D_6 helped establish that one proton of each NH_2 group of **1** is also involved in hydrogen bonding. The ^1H resonances at $\delta = 11.2$ and 5.2 correspond to two protons attached to the same nitrogen atom. The inequivalence of these two amino protons and the large separation between the signals ($\Delta\delta = 6$) is consistent with rotation about the $C-NH_2$ bond being slow on the NMR time scale. Such a slow bond rotation is easily rationalized in terms of a strong hydrogen bond involving one of the two amino protons. On the basis of literature precedent,[4] the resonance at $\delta = 11.2$ is ascribed to the proton that is hydrogen-bonded, while that at $\delta = 5.2$ is assigned to the "free" proton.

A similar separation of the signals for the two amino NH_2 protons is not seen for **2** in $CDCl_3$. Instead, a weak, very broad, upfield-shifted signal ($\delta \approx 5.5$) is observed. We therefore concluded that the NH_2 groups in **2** do not participate in the self-association process.[13] Rather, **2** self-associates in $CDCl_3$ to form dimer **II** as a result of hydrogen-bonding interactions that involve solely the two CO/NH moieties.[14]

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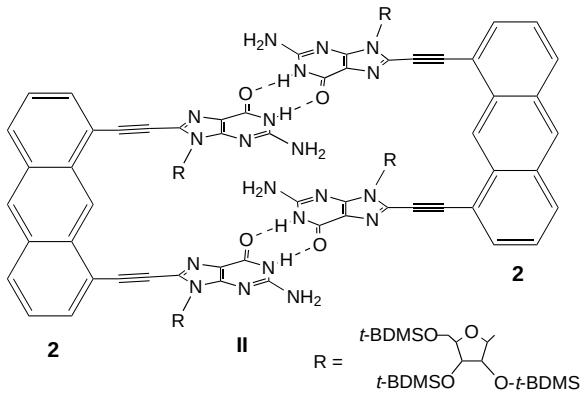

Further insights into the structure of ensemble **I** were obtained from 2D ROESY experiments.[15] Specifically, these revealed distinct correlations between H1″ of the sugar at $\delta =$ 6.7 and H9 of the anthracene moiety at $\delta = 9.8$, as well as between the N=CH proton at $\delta = 9.1$ and the two protons H5″ of the sugar at $\delta = 5.3$ and 3.9 (Figure 1). These results are consistent with the glycoside bond being in the *syn* conformation.[16]

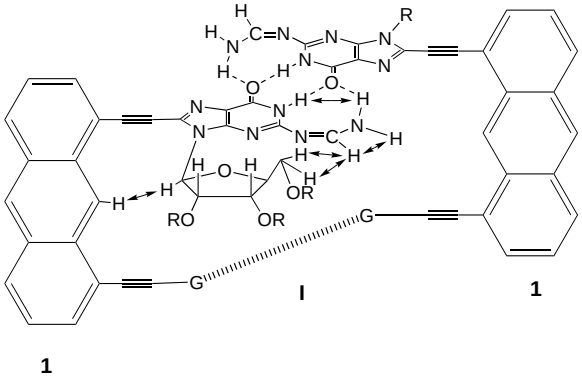

Figure 1. Schematic representation of the significant NOE interactions (indicated by arrows) deduced from the 2D ROESY spectrum of **1**. For clarity, only a part of the overall structure is shown in detail (G = guanyl substituent).

The ROESY experiments also revealed 1) a strong interaction between the imino NH protons ($\delta = 13.6$) and the hydrogen-bonded proton ($\delta = 11.2$) of the exocyclic NH_2 group, 2) a much weaker correlation between the imino NH and N=CH protons ($\delta = 9.1$), and 3) no correlation between the imino NH proton and the non-hydrogen-bonded proton of NH_2 ($\delta = 5.2$). An intense correlation for the ROESY interaction between the N=CH proton and the free proton of NH_2 as well as a much weaker correlation between the N=CH proton and the hydrogen-bonded NH_2 proton were also observed. These findings, when considered in concert, are consistent with the N=C bond existing in a *cis* configuration.

Finally, the ROESY analyses revealed an intense correlation for the interaction between the imino NH proton and the hydrogen-bonded NH_2 proton. Therefore, they must be hydrogen-bonded to the same carbonyl oxygen atom.[7b] Certainly, the *cis* configuration of the N=C bond acts to position the amino group much closer to the carbonyl oxygen atom than to N7; this was also shown by CPK model studies.[17]

With respect to the stability of dimer **I**, we were quite surprised to find that it remains intact under *all* solution-phase conditions tested. Indeed, attempts to measure binding constants for the $\mathbf{1} \rightleftharpoons 1/2\,\mathbf{I}$ dimerization failed due to the simple fact that we were unable to effect appreciable dissociation. For instance, dilution experiments carried out in CD_2Cl_2 did not give rise to any signals in the ^{1}H NMR spectrum that could be ascribed to free **1**. Indeed, the chemical shifts of both the imino NH and amino NH_2 protons were not only independent of concentration in nonpolar solvents such as CD_2Cl_2 and C_6D_6, they were also insensitive to temperature changes from 298 – 398 °C (solvent: [D_8]toluene). Attempts to use polar solvents such as [D_6]DMSO to break up the hydrogen-bonded ensemble[18] also failed.[19] While adding [D_6]DMSO to a solution of **1** in [D_8]toluene did give rise to complex splitting patterns, detailed analyses revealed that these induced changes were due to the formation of DMSO adducts rather than dissociation. By contrast, ensemble **II** completely dissociated at room temperature in [D_6]DMSO/$CDCl_3$ (7/3). Under these conditions, the chemical shifts of the imino NH and amino NH_2 protons appear at $\delta = 10.6$ and 6.4, respectively. These values are incidentally identical to those recorded in pure [D_6]DMSO. Thus, like a system we reported earlier with two-point hydrogen bonds,[18] **II** constitutes a well-defined dimer that can nonetheless be cleaved to form the monomers.

NMR spectroscopic studies at various temperatures and in different polar solvent mixtures indicated that the set of individual resonances ($\delta = 13.6$ and 11.2) observed for the room-temperature ^{1}H NMR spectrum of **1** in [D_8]toluene appears in the form of a pair of doublets (centered at $\delta = 13.5$ and 10.6) when the same measurements are made in [D_6]DMSO/[D_8]toluene (1/1). The two doublets coalesce into singlets at 57 °C and remain as such as the temperature is further increased. An ^{1}H – ^{15}N HMQC NMR experiment for the same sample conducted at 100 °C in the same solvent served to identify the resonances from the imino NH proton and the two amino NH_2 protons; it was thus possible to deduce that the chemical shifts of the imino NH proton and of the hydrogen-bonded NH_2 proton are but slightly changed (both are shifted upfield by $\Delta\delta \approx 0.7$) upon passing from pure [D_8]toluene to [D_6]DMSO/[D_8]toluene (1/1). In marked contrast, the resonance of the free NH_2 proton is shifted downfield by $\Delta\delta \approx 3$ when the same change in solvent is effected. This leads us to suggest that the basic hydrogen-bonded structure of **I** is largely intact even in [D_6]DMSO/[D_8]toluene (1/1). Under these conditions the free protons of NH_2 interact with the [D_6]DMSO solvent; this causes their magnetic environment to be greatly perturbed.[20] Such interactions do not, however, effect break up of the dimer.

Experimental Section

6: To a mixture of **3** (1.5 g, 6.6 mmol), **5** (10.0 g, 13.2 mmol), and *n*BuSnOMe (4 mL, 14 mmol) in dry toluene (100 mL) was added bis(triphenylphosphane)palladium(II) chloride (0.75 g, 8 mol%) under argon. The mixture was heated at 100 °C for 20 h. The solvent was removed under reduced pressure with a rotary evaporator, and the residue was subjected to

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chromatography on a silica gel column with MeOH/ethyl acetate (5/95) as eluent to give **6** (3.4 g, 32 % yield).

1: Compound **6** (3.0 g, 1.9 mmol) was treated with methanolic ammonia (50 mL) and stirred at room temperature overnight. After chromatographic purification on silica gel with hexane/ethyl acetate (4/1) as eluent, **1** was obtained as a fluorescent yellow solid (2.3 g, 80 % yield). ^{1}H NMR (500 MHz, C_6H_6): $\delta = 13.63$ (s, 2H, NH), 11.22 (d, $J = 14.2$ Hz, 2H, NH_2), 9.83 (s, 1H, H9), 9.12 (dd, $J = 5.3$, 14.2 Hz, 2H, N=CH), 8.12 (s, 1H, H10), 7.71 (d, $J = 8.9$ Hz, 2H, H4, H5), 7.53 (d, $J = 6.89$ Hz, 2H, H2, H7), 7.06 (dd, $J = 8.7$, 6.7 Hz, 2H, H3, H6), 6.67 (d, $J = 8.15$ Hz, 2H, H1′), 5.33 – 5.31 (m, 4H, H2′, H5′), 5.29 (br s, 2H, NH_2), 4.47 – 4.44 (m, 4H, H3′, H4′), 3.98 – 3.88 (m, 2H, H5′), 1.67 – 0.53 (ss, 90H, $6\,Si(CH_3)_2C(CH_3)_3$); ^{13}C NMR (125 MHz, C_6H_6): $\delta = 160.3$ (C6′), 160.1 (N=CH), 156.5 (C2′), 150.7 (C4′), 136.1, 133.1, 132.0 (aromatic C), 131.6 (C2), 129.9 (C4), 128.3 (C10), 125.2 (C3), 124.1 (C9), 122.0 (C8′), 120.1 (C5′), 92.5 (alkynyl C), 87.9 (C1″), 85.9 (alkynyl C), 85.7 (C4″), 74.4 (C3″), 71.8 (C2“), 64.5 (C5″), 26.6, 25.9, 25.0 ($SiMe_2C(CH_3)_3$), 18.6, 18.1, 17.5 ($SiMe_2CMe_3$), −4.4, −4.6, −4.7, −4.8, −5.3 ($Si(CH_3)_2CMe_3$); FAB-MS: *m*/*z* 1527 [M^+]; high-resolution FAB-MS calcd for $C_{76}H_{119}N_{12}O_{10}Si_6$: 1527.7788 [$M^+$ of **1**], found: 1527.7752; FAB-MS 3054; high-resolution FAB-MS calcd for $C_{152}H_{238}N_{24}O_{20}Si_{12}$: 3054.550 ($M^+$ of the dimer), found: 3054.549; elemental analysis calcd for $C_{76}H_{119}N_{12}O_{10}Si_6$: C 59.73, H 7.79, N 11.01; found C 59.74, H 7.69, N 10.86.

2: Compound **1** (0.3 g, 0.2 mmol) was treated with ammonia saturated in methanol/$CHCl_3$ (1/1, 20 mL) at 100 °C in a sealed tube overnight. The solvents were removed under reduced pressure with a rotary evaporator, and the residue was subjected to chromatography on a silica gel column with MeOH/$CHCl_3$ (7/93) as eluent to give **2** (0.15 g, 52 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 12.65$ (s, 2H), 9.33 (s, 1H), 8.57 (s, 1H), 8.14 (d, $J =$ 8.7 Hz, 2H), 7.92 (d, $J = 6.6$ Hz, 2H), 7.54 (t, $J = 8.1$ Hz, 2H), 6.13 (d, $J =$ 5.1 Hz, 2H), 5.50 (br, 4H), 5.19 (m, 2H), 4.13 (d, $J = 3.9$ Hz, 2H), 3.83 (m, 6H), 0.96 – 0.63 (m, 90H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.1$, 153.4, 151.8, 133.1, 131.9, 131.5, 131.2, 130.8, 128.3, 125.4, 124.0, 119.0, 116.8, 93.4, 88.8, 86.4, 82.6, 73.3, 71.0, 62.7, 25.9, 25.6, 24.9, 18.01, 17.8, 17.7, −4.6, −4.7, −4.9, −5.9, −6.0, −6.4; CI-MS: *m*/*z* 1472 [M^+]; high-resolution CI-MS calcd for $C_{74}H_{116}N_{10}O_{10}Si_6$: 1472.7492 [$M^+$] of **2**; found: 1472.7477.

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[10] A weak signal ascribable to a dimeric species was observed in the mass spectrum of **2**. However, the signal in question was not sufficiently intense to allow for a high-resolution analysis.
[11] The assignment of the resonances in the ^{1}H NMR spectrum of **1** is based on information gleaned from the COSY and HMQC NMR spectroscopic analyses (^{1}H – ^{13}C and ^{1}H – ^{15}N).
[12] Similar shifts were also observed in C_6D_6 and [D_8]toluene. Unfortunately, **2**, **6**, and **7** are insoluble in these solvents. Thus, initial comparative analyses were carried out in $CDCl_3$.
[13] The broad ^{1}H NMR signal for the amino groups of **2** in $CDCl_3$ is due to fast exchange between the two free NH_2 protons. Further support for this conclusion came from the observation that sharp signals, ascribable to the amino groups in question, were seen in the ^{1}H NMR spectra of both **7** in $CDCl_3$ (where no proton is available for exchange) and **2** in [D_6]DMSO (where both NH_2 protons are hydrogen-bonded to [D_6]DMSO).
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[15] Several features of 2D ROESY spectrum of **1** in C_6D_6 are noteworthy. First, the intense cross peaks observed between H1″ at $\delta = 6.7$ and H9 at $\delta = 9.8$ as well as between N=CH at $\delta = 9.1$ and H5″ at $\delta = 5.3$ and 3.9 provide evidence for the *syn* conformation of the glycoside bond. Secondly, the observation of intense cross peaks between the imino NH proton at $\delta = 13.6$ and the hydrogen-bonded proton of NH_2 at $\delta =$ 11.2, coupled with presence of a much weaker cross peak involving this imino NH proton and the N=CH proton and no cross peak with the non-hydrogen-bonded proton of NH_2 at $\delta = 5.2$, provide evidence for the *cis* configuration of the N=CH bond. Finally, the intense cross peak observed between the signals at $\delta = 13.6$ for the imino NH proton and at $\delta = 11.2$ for the hydrogen-bonded NH_2 proton provides evidence of close proximity of these two protons.
[16] a) The *syn* conformation is also believed to play a critical role during the synthesis because only it allows the 8-position to be most susceptible to nucleophilic attack by its coupling partner; b) both a *syn* conformation of the glycosidic bond and a *cis* configuration of the C=N bond are assigned to **6** on the basis of NMR spectral similarities.
[17] The fact that the lone pairs of the two carbonyl oxygen atoms are tied up in hydrogen bonding is believed to contribute to the nonpolarity of **1**.
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[19] The insolubility of **1** under the conditions of the experiment precluded the use of the more strongly hydrogen bonding solvent water.
[20] The coalescence observed at higher temperature is the result of fast exchanges between different states of DMSO-derived solvation of the four amino protons. This gives rise to an average chemical shift for these protons; at lower temperature, however, the relevant exchange processes are slow enough on the NMR time scale that multiple resonances are observed.

Tethered Bis-Amidinates as Supporting Ligands: A Concerted Elimination/σ – π Rearrangement Reaction Forming an Unusual Titanium Arene Complex**

John R. Hagadorn and John Arnold*

Development of ligands that play supporting roles in organotransition metal chemistry has been the subject of intense interest for many years. We are exploring amidinates in this regard as they display attractive properties from a synthetic standpoint. Well characterized titanium derivatives, that utilized the *N*,*N*′-bis(trimethylsilyl)benzamidinate li-

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