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Supporting Information

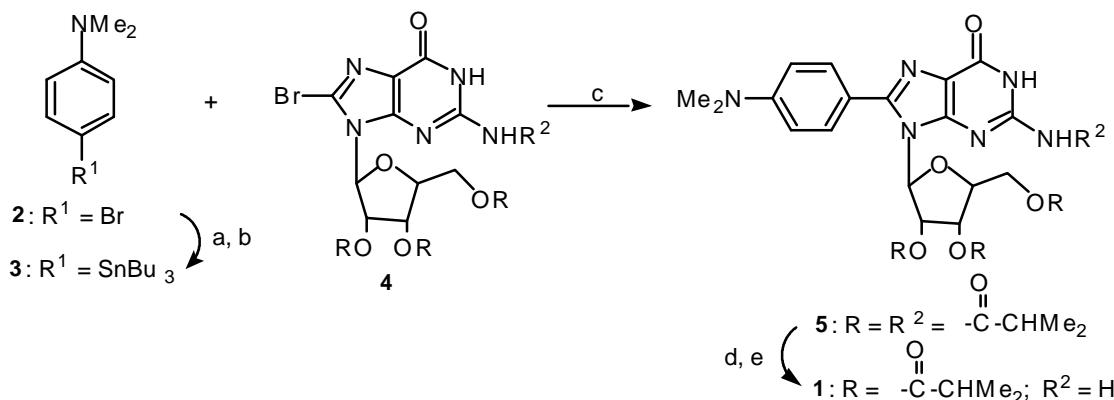
**A G-Quartet Formed in the Absence of Templating Metal Cation:
Synthesis, X-ray Crystal Structure and Solution Studies of a New 8-
(*N,N*-dimethylaniline)guanosine Derivative.**

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Complete experimental procedures, spectral and analytical data for products, VPO analysis of **1** and NMR analysis of (2',3',5'-tri-*O*-isobutyrylribofuranosidyl)-2-aminopurin-6-one.

To be Published as Electronic Supplementary Material

Experimental Section



a. BuLi, THF, -78 °C; b. Bu_3SnCl , -78 °C → rt., 90%; c. $Pd(PPh_3)_4$, toluene, reflux, 95%; d. NH_3 , MeOH, CH_2Cl_2 ; e. $(Me_2CHCO)_2O$, DMAP, TEA, MeCN, 50%.

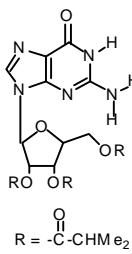
N,N-Dimethyl-4-(tri-n-butylstannylyl)aniline 3:^[1] To a solution of 4-bromo-*N,N*-dimethylaniline **2** (2 g, 10 mmol) in dry THF (50 mL) at -78 °C under argon was added slowly a solution of BuLi (1.6 M in hexane, 7 mL, 12 mmol). The resulting white suspension was stirred at -78 °C for 30 min. To this suspension was then added tri-*n*-butyltinchloride (3.25 g, 10 mmol). The resulting clear solution was then allowed to warm to rt. The solution was poured into diethyl ether (100 mL), washed with 5% $NaHCO_3$ (100 mL), brine (100 mL), dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and then dried under vacuum. The crude product **3** (3.7 g, 90%) pure as judged from NMR, was used in the next step without further purification. 1H -NMR (300 MHz; C_6D_6): δ = 0.92 (t, J = 7.3 Hz, 9H), 1.13 (t, J = 8.1 Hz, 6H), 1.36-1.44 (m, 6H), 1.64-1.70 (m, 6H), 2.55 (s, 6H), 6.71 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H); ^{13}C -NMR (75.5 MHz; C_6D_6): δ = 9.93, 13.93, 28.81, 29.67, 40.03, 113.36, 126.41, 137.51, 150.45.

8-(4''-N,N-Dimethylanilinyl)-9-(2',3',5'-tri-O-isobutyrylribosidyl)-2-isobutyrylamidopurin-6-one (5): A solution of **3** (13.1 g, 33 mmol) and 8-bromo-9-(2',3',5'-tri-O-isobutyrylribosidyl)-2-isobutyrylamidopurin-6-one (**4**)^[2] (6.4 g, 10 mmol) in dry toluene (200 mL) was purged with argon for 20 min. To this solution $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) was added at once and the resulting solution was heated at reflux under argon for 12 h. After cooling, and evaporation on to silica gel, flash column chromatography (silica gel, eluent 1:1 EtOAc/hexane followed by 2:1 EtOAc/hexane) afforded **5** in 80% yield (5.5 g). 1H -NMR (300 MHz; CD_2Cl_2): δ = 1.05-1.20 (m, 18H), 1.30-1.70 (m, 6H), 2.45-2.65 (m, 3H), 2.75 (sept. J = 6.9 Hz, 1H), 3.04 (s, 6H), 4.43 (dd, J = 11.9, 5.7 Hz, 1H), 4.43-4.46 (m, 1H), 4.62 (dd, J = 11.9, 4.3 Hz, 1H), 5.95 (d, J = 3.2 Hz, 1H), 6.23 (dd, J = 5.0, 3.2 Hz), 6.31 (dd, J = 6.7, 5.0 Hz, 1H), 6.8 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 9.12 (bs, 1H), 11.85 (bs, 1H); ^{13}C -NMR (75.5 MHz; $CDCl_3$): δ = 18.37, 18.53, 18.69, 33.44, 33.56, 33.60, 36.20, 39.83, 62.22, 70.64, 72.38, 78.42, 87.51, 111.38, 115.71, 121.03, 130.30, 146.31, 148.08, 150.95, 151.12, 155.22, 175.15, 176.03, 176.88, 178.46; HRMS-CI [M+1]⁺: calcd. 683.3405; found 683.3394.

8-(4''-N,N-Dimethylanilinyl)-9-(2',3',5'-tri-O-isobutyrylribosidyl)-2-aminopurin-6-one (1): An ice cold mixture of MeOH: CH_2Cl_2 (2:1; 300 mL) was saturated with ammonia gas. This saturation procedure was repeated twice. To this solution was added **5** (2.5 g, 3.7 mmol). The resulting clear solution was then stirred at rt. for 36 h in a sealed flask. The solvents were evaporated off in vacuo and the resulting solid was dried at 45 °C for 24 h. To the suspension of

dried residue in dry acetonitrile (100 mL) was added isobutyric anhydride (2 g, 12.8 mmol), triethylamine (1.3 g, 12.8 mmol), and DMAP (0.05 g, 0.41 mmol). The resulting suspension was stirred at rt. for 30 min. After this period, an excess of MeOH was added and the resulting solution stirred for an additional 10 min. The solution that resulted was then concentrated in vacuo. The crude product obtained this way was purified by flash column chromatography (silica gel, eluent $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 1:2) to afford **1** (1.5 g, 67%). $^1\text{H-NMR}$ (300 MHz; CD_2Cl_2): δ = 1.0 – 1.2 (m, 18H), 2.48 – 2.6 (m, 3H), 3.07 (s, 3H), 4.3 – 4.34 (m, 2H), 4.48 (dd, J = 5.8, 14.0 Hz, 1H), 5.9 (d, J = 3.5 Hz, 1H), 6.15 (t, J = 5.7 Hz, 1H), 6.32 (t, J = 4.4 Hz, 1H), 6.86 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 12.31 (bs, 1H); $^{13}\text{C-NMR}$ (75.5 MHz; CD_2Cl_2): δ = 8.63, 8.72, 8.78, 8.87, 23.87, 23.97, 30.10, 52.69, 60.40, 62.38, 69.29, 77.85, 102.08, 105.98, 106.48, 120.29, 139.83, 141.69, 142.45, 143.55, 149.40, 165.51, 165.66, 166.74; HRMS-Cl ($M+1$): calcd. 613.2986, found 613.2999; Anal. calcd. $\text{C}_{30}\text{H}_{40}\text{N}_6\text{O}_8 \cdot (\text{CH}_2\text{Cl}_2)_{1/3}$: C, 56.84; H, 6.39; N, 13.11; found: C, 56.76; H, 6.54; N, 13.16.

9-(2',3',5'-tri-O-isobutyrylribofuranosidyl)-2-aminopurin-6-one: To a suspension of guanosine hydrate (1.4 g, 5.0 mmol) in dry acetonitrile (30 mL) were added isobutyric anhydride (2.6 mL, 16 mmol), triethyl amine (2.3 mL, 16 mmol) and DMAP (0.06 g, 0.5 mmol). The resulting suspension was stirred at rt. for 10 min. After this period an excess of MeOH was added and stirred for an additional 5 min. The solution was concentrated in vacuo. The crude product obtained this way was then purified by flash column chromatography (silica gel, eluent $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$

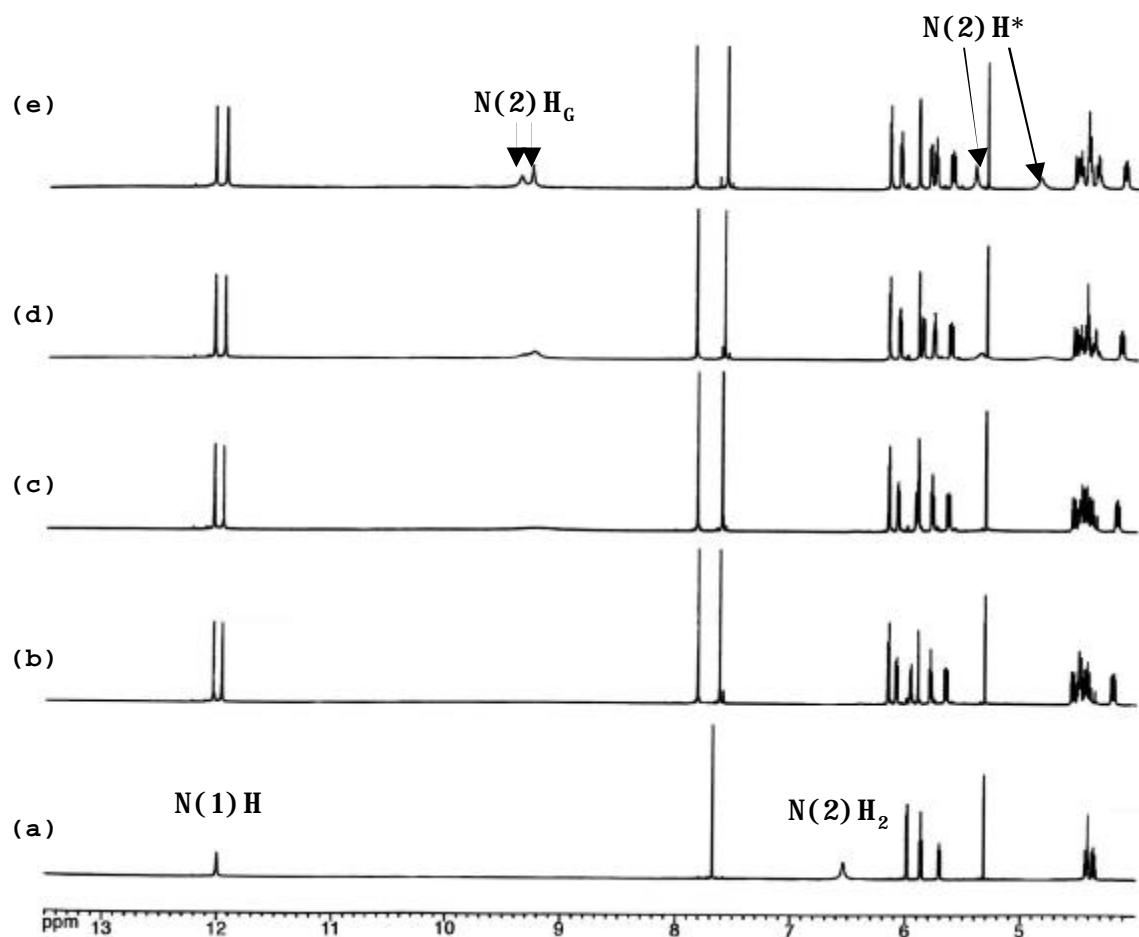
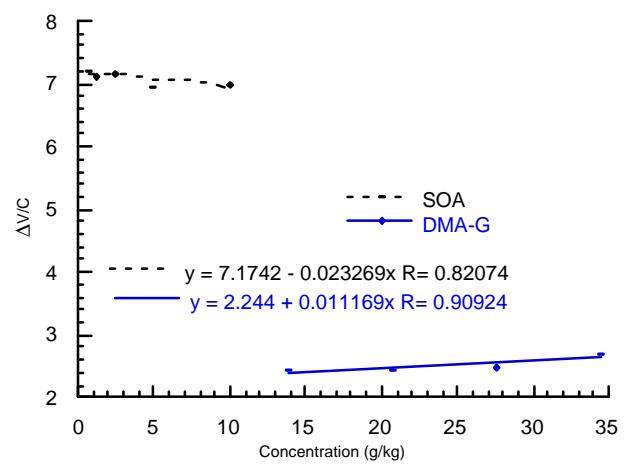


1:3) to afford the desired compound (2.4 g, 96%). HRMS-Cl calcd. 494.2251, found 494.2246.

Vapor Pressure Osmometry:^[3]

Vapor pressure osmometry measurements of **1** were carried out on a Jupiter Instruments Model 833, vertical-thermistor type vapor pressure osmometer. Triply recrystallized sucrose octaacetate was used as the standard and all the measurements were carried out in HPLC grade dichloroethane. The CELL and the SYRINGE temperatures were held at 40 C and rt. respectively. The RANGE switch and CURRENT switches were set at 2 mV and 20 μ A respectively. The instrument constant (K) was calculated from the intercept of a calibrating sucrose octaacetate plot. This was then used to calculate the number averaged molecular weight of the DMA-G aggregate. $K = 7.1742 * 678.6 = 4870$; $M_n = 4870/2.244 = 2170 \pm 150$ amu.

The graph below shows the concentration dependence of the equilibrium voltage, during the VPO experiment, for the solutes. A sucrose octaacetate (SOA) plot was used to calculate the instrument constant, which was then used to calculate the molecular weight of the putative of **1** aggregate. As described in the text proper, these results are consistent with the formation of a self-assembled tetramer.



¹H-NMR of (2',3',5'-tri-*O*-isobutyrylribofuranosidyl)-2-aminopurinone:

(a) 40 mM solution of in CD₂Cl₂ at 27 C; (b) - (e) 40 mM solution with 8:1 equivalent KI at 27, 15, 0, and -15 C respectively.

References

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- [3] a) Burge, D. E. *American Laboratory* **1977**, *9*, June 41-51; b) Burge, D. E. *J. Appl. Polym. Sci.* **1979**, *24*, 293-299.