Online supporting material

Synthesis and characterization of the substituted adenines

9-acetyladenine

9-acetyladenine was synthesized by adding a mixture of anhydrous dimethyl sulfoxide (25 mL), anhydrous pyridine (10 mL), and acetic anhydride (2.5 mL) to a solution of adenine (670 mg, 5.00 mmol) . The reaction mixture was stirred at room temperature for 24 h. The mixture was filtered and the precipitate was washed with cold pyridine and diethyl ether. After recrystallization from water and ethanol 9-acetyladenine (489 mg, 55%) was obtained as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (s, 3 H), 7.52 (br, 2 H), 8.28 (s, 1 H), 8.61 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.8 (CH_3), 119.5 (C_{quat}), 138.4 (CH), 148.7 (C_{quat}), 153.9 (CH), 156.4 (C_{quat}), 168.4 (C_{quat}). EI (70 eV) m/z (%): 177 (M^+, 1), 135 (M^+ - C_2H_2O, 100), 108 ($C_4H_4N_4^+$, 55), 54 ($C_2H_2N_2^+$, 22), 43 (CH_3CO^+, 73). Anal. calcd. for $C_7H_7N_5O$ (177.2): C 47.46, H 3.98, N 39.53; Found: C 47.24, H 3.91, N 39.26. Mp.: $>$ 250 °C.

9-(n-butyl)adenine

9-(n-butyl)adenine was synthesized by mixing 500 mg of adenine (3.70 mmol), 1.46 g of cesium carbonate (4.50 mmol), 0.825 mg of 1-iodobutane (4.50 mmol), and 20 mL of dimethylformamide in a Schlenk flask. The reaction mixture was stirred at 50 °C for 24 h and then diluted with water (50 mL). All solvents were removed in vacuo and the residue was purified by flash chromatography (chloroform/methanol/ammonia 90:10:1) to give 9-butyladenine (376 mg, 52 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.95 (m, 3 H), 1.34 (m, 2 H), 1.85 (m, 2 H), 4.22 (m, 2 H), 8.12 (s, 1 H), 8.20 (s, 1 H). ^{13}C NMR (125 MHz, d^6-DMSO): δ 13.4 (CH_3), 19.2 (CH_2), 31.3 (CH_2), 42.6 (CH_2), 118.7 (C_{quat}), 140.8 (CH), 149.5 (C_{quat}), 152.3 (CH), 155.9 (C_{quat}). EI (70 eV) m/z (%): 192 (4), 191 (M^+, 32), 148 (M^+ - C_3H_7, 100), 135 (M^+ - C_4H_8, 35), 108 ($C_4H_4N_4^+$, 17).

9-methyladenine

In a round bottom flask tetra-n-butylammoniumhydroxid tridecahydrate (4.89 g, 6.10 mmol) was dissolved in distilled water (10 mL). To this solution adenine (0.83 g, 6.00 mmol) was added at room temperature and the reaction mixture was stirred until the adenine was completely dissolved. Then, a solution of iodomethane (1.70 g, 12.1 mmol) in dichloromethane (15 mL) was added and the resulting mixture was heavily stirred over night at room temperature. All solvents were removed in vacuo and the residue was purified by flash chromatography (chloroform/methanol/ammonia 90:10:1) to give 9-methyladenine (247 mg, 28 %) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.48 (s, 3 H), 7.65 (s, 1 H), 7.67 (s, 1 H). EI (70 eV), m/z (%): 149 (M^+, 100), 122 (M^+ - HCN, 30), 68 (M^+ - 3 HCN, 12), 42 (H_2NCN^+, 42). Anal. calcd. for $C_6H_7N_5$ (149.2): C 48.32, H 4.73, N 46.95; Found: C 48.31, H 4.77, N 46.65. Mp.: $>$ 250 °C.

2,8-dideutero-9-methyladenine

9-methyladenine (66 mg, 0.4 mmol) was mixed with palladium on charcoal (6.7 mg, 10 mol%), and D_2O (1 mL) in a Schlenk flask. After degassing the mixture with hydrogen for 10 min, the Schlenk flask was sealed and placed with stirring in an oil bath reactor at 160 C for 24 h. After cooling to room temperature the mixture was filtered and the catalyst was washed with boiling water. After removing the water in vacuo 2,8-dideutero-9-methyladenine (61 mg, 92%) was obtained as colorless crystals.

^{1}H NMR (500 MHz, D_2O): δ 3.69 (s, 3H).

R2PI spectra of all investigated adenine derivatives

Figure S1 shows the two-color R2PI spectra of (a) 9H-adenine, (b) 9-methyladenine, (c) 2,8-deutero-9-methyladenine, (d) 9-ethyladenine, (e) 9-(n-butyl)adenine, and (f) 9-acetyladenine.

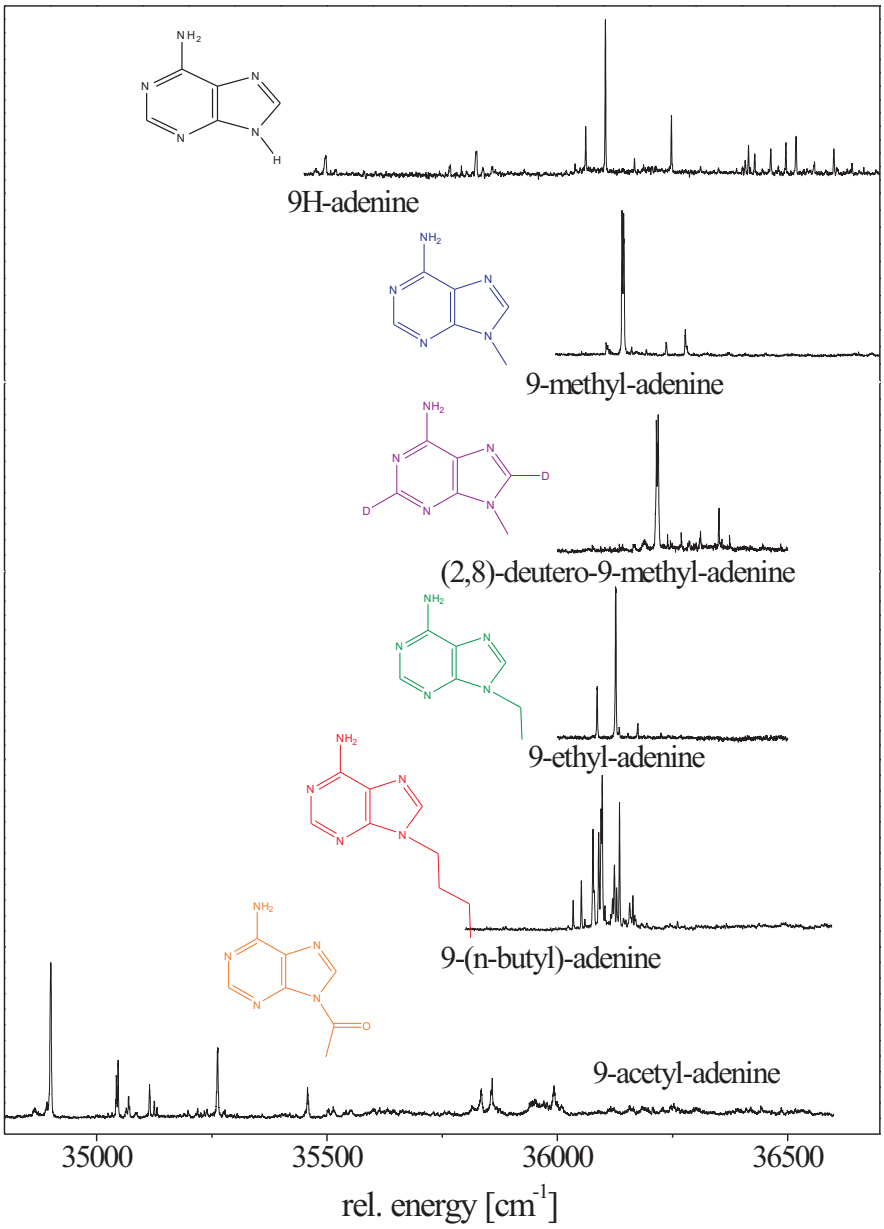

Figure S1: Two-color R2PI spectra of (a) 9H-adenine, (b) 9-methyladenine, (c) 2,8-deutero-9-methyladenine, (d) 9-ethyladenine, (e) 9-(n-butyl)adenine, and (f) 9-acetyladenine.

Rovibronic contours of the $n\pi^*$ and $\pi\pi^*$ origin bands of 9H-adenine.

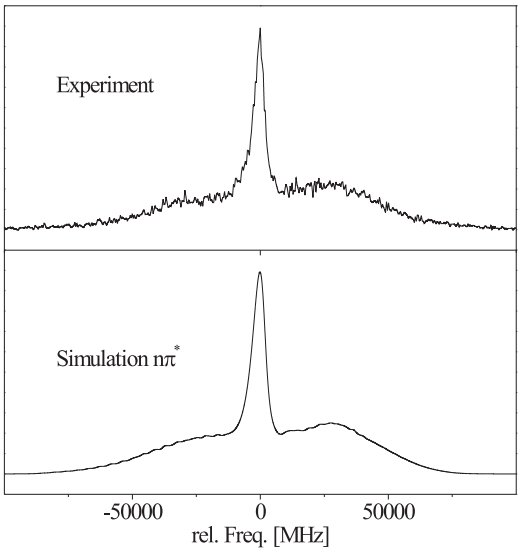

Figure S2: Experimental rovibronic contour from Ref. [1] and simulation of the $n\pi^*$ origin band of 9H-adenine using the rotational constants from the CC2/cc-pVTZ optimized structures and the transition moment orientations from DFT/MRCI calculations based on the CC2 structures.

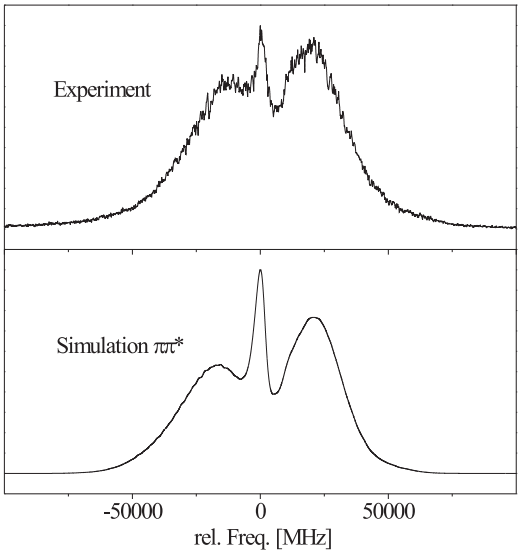

Figure S3: Experimental rovibronic contour from Ref. [1] and simulation of the $\pi\pi^*$ origin band of 9H-adenine using the rotational constants from the CC2/cc-pVTZ optimized structures and the transition moment orientations from DFT/MRCI calculations based on the CC2 structures.

Geometry parameters from the structure optimizations

9H-adenine

Table S1: Bond distances r [pm] and selected dihedral angles θ [deg] for the equilibrium geometries of several electronic states of 9H-adenine. (CC2/cc-pVTZ)

coordinate	S_0	$^1(n \rightarrow \pi^*)$	$^1(\pi \rightarrow \pi^*)$
$r(\mathrm{C_6}-\mathrm{N_1})$	134.3	131.4	131.4
$r(\mathrm{N_1}-\mathrm{C_2})$	134.9	137.6	137.6
$r(\mathrm{C_2}-\mathrm{N_3})$	134.1	142.0	142.1
$r(\mathrm{N_3}-\mathrm{C_4})$	134.0	132.2	132.2
$r(\mathrm{C_4}-\mathrm{C_5})$	139.9	141.6	141.8
$r(\mathrm{C_5}-\mathrm{C_6})$	140.5	143.7	143.7
$r(\mathrm{C_5}-\mathrm{N_7})$	138.3	135.2	135.3
$r(\mathrm{N_7}-\mathrm{C_8})$	132.3	132.9	132.8
$r(\mathrm{C_8}-\mathrm{N_9})$	137.4	140.2	140.2
$r(\mathrm{N_9}-\mathrm{C_4})$	137.6	136.8	136.9
$r(\mathrm{C_6}-\mathrm{N_{10}})$	135.9	137.7	137.7
$\theta(\mathrm{N_1}-\mathrm{C_6}-\mathrm{C_5}-\mathrm{C_4})$	-0.4	-0.1	-0.2
$\theta(\mathrm{N_3}-\mathrm{C_4}-\mathrm{C_5}-\mathrm{C_6})$	0.1	-1.3	-1.5
$\theta(\mathrm{C_2}-\mathrm{N_3}-\mathrm{C_4}-\mathrm{C_5})$	0.1	12.9	13.2
$\theta(\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{C_5}-\mathrm{N_7})$	-3.0	-2.4	-2.8
$\theta(\mathrm{H_{11}}-\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{C_5})$	17.8	20.4	20.6
$\theta(\mathrm{H_{12}}-\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{N_1})$	-16.9	-27.2	-27.0
$\theta(\mathrm{H_{13}}-\mathrm{C_2}-\mathrm{N_3}-\mathrm{C_4})$	179.7	-164.3	-164.4
$\theta(\mathrm{H_{14}}-\mathrm{N_9}-\mathrm{C_4}-\mathrm{C_5})$	179.7	-179.6	-178.2
$\theta(\mathrm{H_{15}}-\mathrm{C_8}-\mathrm{N_7}-\mathrm{C_5})$	-1.8	-179.1	-179.0

9-acetyladenine

Table S2: Bond distances r [pm] and selected dihedral angles θ [deg] for the equilibrium geometries of several electronic states of 9-acetyl-adenine. (CC2/cc-pVTZ)

coordinate	S_0	$^1(n \rightarrow \pi^*)$	$^1(\pi \rightarrow \pi^*)$
$r(\mathrm{C_6}-\mathrm{N_1})$	134.6	134.5	131.5
$r(\mathrm{N_1}-\mathrm{C_2})$	134.5	134.7	136.8
$r(\mathrm{C_2}-\mathrm{N_3})$	134.5	134.3	139.3
$r(\mathrm{N_3}-\mathrm{C_4})$	134.0	133.9	131.3
$r(\mathrm{C_4}-\mathrm{C_5})$	139.7	139.7	142.8
$r(\mathrm{C_5}-\mathrm{C_6})$	140.4	140.6	143.9
$r(\mathrm{C_5}-\mathrm{N_7})$	138.7	138.3	133.8
$r(\mathrm{N_7}-\mathrm{C_8})$	131.5	132.1	133.5
$r(\mathrm{C_8}-\mathrm{N_9})$	139.3	139.5	142.3
$r(\mathrm{N_9}-\mathrm{C_4})$	139.7	139.8	139.0
$r(\mathrm{C_6}-\mathrm{N_{10}})$	135.5	135.5	137.1
$r(\mathrm{N_9}-\mathrm{C_{11}})$	143.1	137.2	141.1
$r(\mathrm{C_{11}}-\mathrm{O_{12}})$	121.8	145.5	122.5
$r(\mathrm{C_{11}}-\mathrm{C_{13}})$	149.5	147.6	149.8
$\theta(\mathrm{N_1}-\mathrm{C_6}-\mathrm{C_5}-\mathrm{C_4})$	0.6	-0.3	0.1
$\theta(\mathrm{N_3}-\mathrm{C_4}-\mathrm{C_5}-\mathrm{C_6})$	-0.1	-0.3	-1.1
$\theta(\mathrm{C_2}-\mathrm{N_3}-\mathrm{C_4}-\mathrm{C_5})$	-0.2	0.4	8.5
$\theta(\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{C_5}-\mathrm{N_7})$	2.8	-2.3	-2.5
$\theta(\mathrm{H_{14}}-\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{C_5})$	15.5	15.7	19.8
$\theta(\mathrm{H_{15}}-\mathrm{N_{10}}-\mathrm{C_6}-\mathrm{N_1})$	15.2	14.9	25.0
$\theta(\mathrm{H_{16}}-\mathrm{C_2}-\mathrm{N_3}-\mathrm{C_4})$	-179.6	-179.8	-168.8
$\theta(\mathrm{H_{20}}-\mathrm{C_8}-\mathrm{N_7}-\mathrm{C_5})$	180.0	179.9	179.5
$\theta(\mathrm{C_{11}}-\mathrm{N_9}-\mathrm{C_4}-\mathrm{C_5})$	-179.9	-175.5	-179.7
$\theta(\mathrm{O_{12}}-\mathrm{C_{11}}-\mathrm{N_9}-\mathrm{C_4})$	179.8	179.0	179.2
$\theta(\mathrm{C_{13}}-\mathrm{C_{11}}-\mathrm{N_9}-\mathrm{C_4})$	0.2	38.7	-0.9

References

[1] Y. Lee, B. Kim, M. Schmitt, and K. Kleinermanns, *J. Phys. Chem. A*, 2006, **110**, 11819–11823.