

Facilitated Assignment of Adenine H2 Resonances in Oligonucleotides using
Homonuclear Long-range Couplings

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Complete Ref. 15

15. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

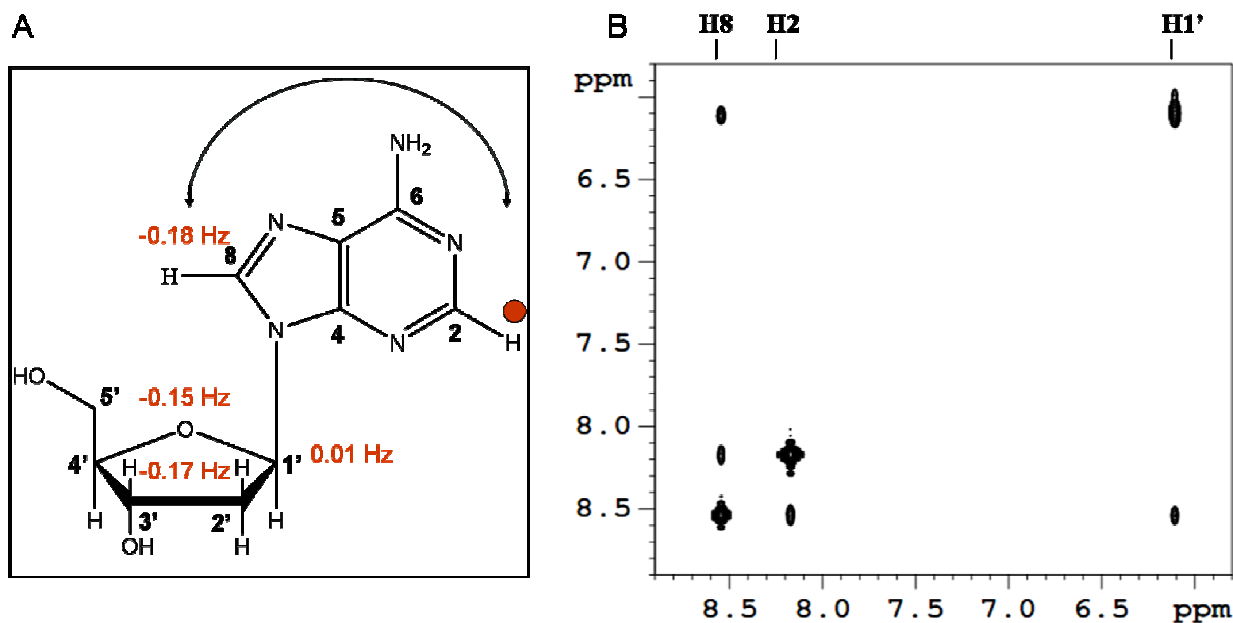


Figure S1. A) DFT spin-spin calculations: 2'-endo deoxyadenosine was optimized with Gaussian03 utilizing HF/6-31G [15]. NMR shielding and spin-spin calculations were obtained using B3LYP and a 6-31G** basis set with the polarizable continuum model and the UA0 cavity for water effects [16, 17]. Couplings from H2 are shown in the figure; couplings from H8 to sugar protons are as follows: H1' (-0.80 Hz) H3' (0.00 Hz) H5' (0.41 Hz), H5'' (0.75 Hz) **B**) 500MHz long range optimized COSY spectrum of a 50mM 5'-AMP sample in 99.99% D₂O, 10 mM sodium phosphate, 0.5 mM EDTA, pH* 6.6 recorded at 298 K with long-range evolution delay of 300 ms and a 10 s relaxation delay. NMR experiments were recorded on Bruker Avance 500 using a 5 mm TBI probe. A 1024 x 128 data point matrix was acquired in a spectral window of 3.0 x 3.0 ppm using 8 scans. Data was processed using a sine window function (SSB = 0) in F1 and F2 and the spectrum is displayed in magnitude mode.

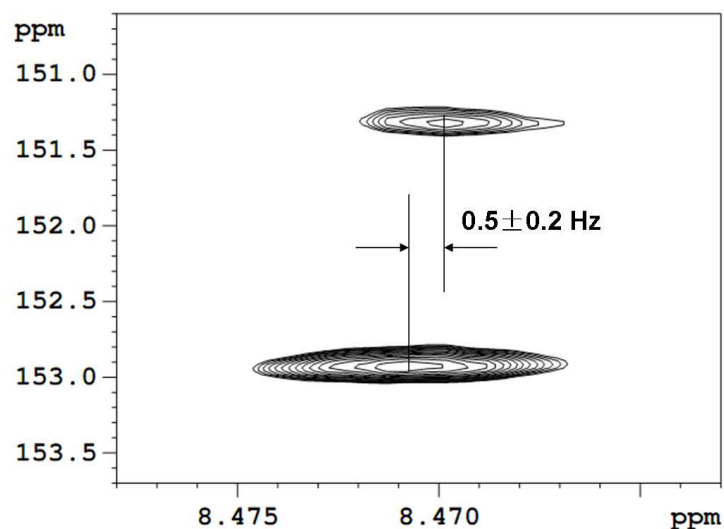


Figure S2. 500 MHz expansion of the XLOC [13] spectrum of a 200mM 5'-AMP in 99.99% D₂O, 10 mM sodium phosphate, 0.5 mM EDTA, pH* 6.6 recorded at 298 K using a first order low-pass J filter with a 1.5 s relaxation delay and an excitation delay of 0.343 s [10]. A 2K x 512 matrix was acquired in a spectral window of 4 x 90 ppm with 16 scans per increment. For processing the window functions were cosine in T₁ and sine in T₂. NMR experiments were recorded on Bruker Avance 500 using a 5mm TBI probe.

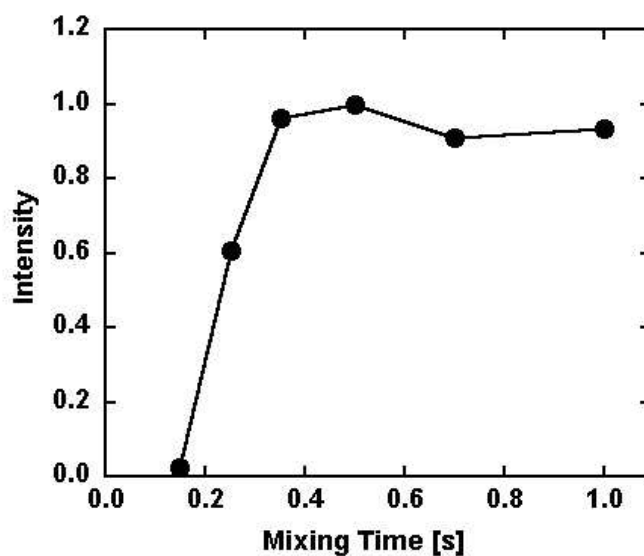


Figure S3. Dependence of cross peak intensity (A6 in Figure 2) on the TOCSY mixing time for the decamer DNA duplex. NMR experiments were recorded on Bruker Avance 600 using a 5mm QXI probe. Transfer H8 (t₁)->H2 (t₂)

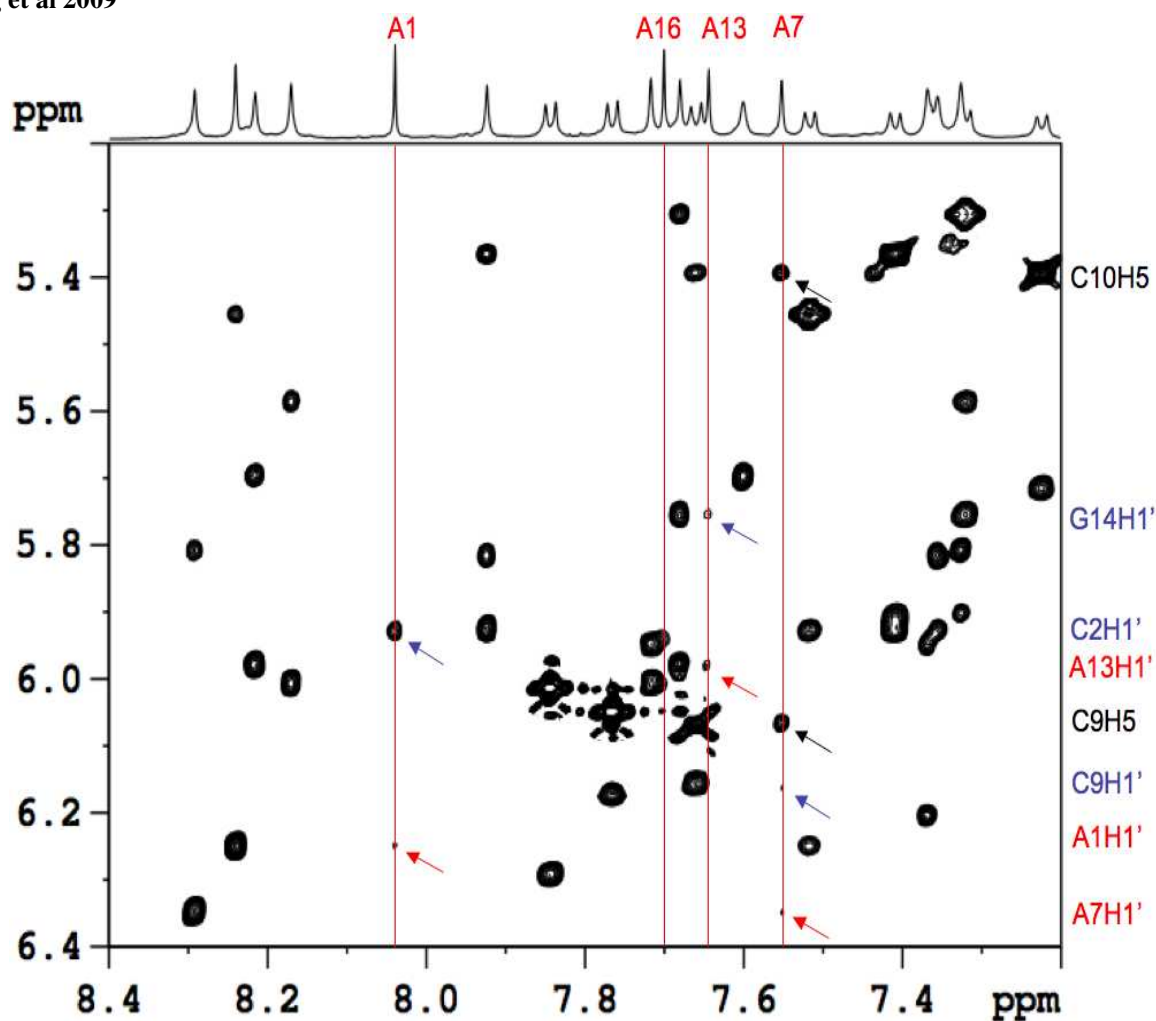


Figure S4 H1'-base region of a 600MHz NOESY spectrum of the 0.75mM hairpin recorded at 298K (99.99% D₂O, 10 mM sodium phosphate buffer, 0.1 mM EDTA 50mM NaCl, pH*6.84) with a mixing time of 200 ms and a relaxation delay of 8 s. Intraresidue H1' connectivities are indicated in red, while cross strand NOE's are show in blue. Black denotes NOE's to loop cytosines. Note that the intraresidue connectivity is very weak and in some cases (A16) absent. For A7, next to the hairpin loop, several weak and several medium NOEs are obtained that are structurally important.