Full author list for reference 52: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., 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.; Pople, J. A. *Gaussian Inc., Wallingford CT.*

Supplementary Quantum Chemical Results. Tables 1S-5S present additional calculated principal components of the anisotropic chemical shift tensors. The structures used for cytidine and guanidine are based on representative nucleotides from the 1QCU X-ray structure of A-form RNA. Specifically, G3 and C14 were chosen as starting points for geometry optimizations. The following torsion angles were held fixed during a partial geometry optimization at the B3LYP/6-311G* level. Guanidine 3: $\nu_0 = 4.1^\circ$, $\nu_1 = -30.9^\circ$; $\nu_2 = 43.7^\circ$, $\nu_3 = -42.6^\circ$, $\nu_4 = 24.4^\circ$, $\chi = -159.1^\circ$, $\alpha = -69.9^\circ$, $\beta = -178.7^\circ$, $\gamma = 49.5^\circ$, $\delta = 79.6^\circ$. Cytidine 14: $\nu_0 = 2.6^\circ$, $\nu_1 = -30.7^\circ$, $\nu_2 = 45.4^\circ$, $\nu_3 = -45.2^\circ$, $\nu_4 = 27.0^\circ$, $\chi = -161.4^\circ$, $\alpha = -69.7^\circ$, $\beta = -179.2^\circ$, $\gamma = 49.1^\circ$, $\delta = 78.9^\circ$. The ε and ζ angles were left undefined as the calculations only involved a single nucleotide (see, e.g., Markley et al., *J. Biomol. NMR* **1998**, *12*, 1-23 for definitions of the torsional angles). The main purpose of the partial optimization was therefore to ensure accurate proton positions with respect to the heavy atoms. The pseudorotation phase (*P*) and amplitude (ψ_m) are 13˚ and 45˚, respectively for the guanidine nucleotide, and 16˚ and 47˚ for the cytidine nucleotide. (See Altona and Sundaralingam, *J. Am. Chem. Soc.* **1972**, *94*, 8205-8212).

Additionally, calculations were performed for a nucleotide near the C1'-exo conformation (G27 of PDB entry 1F27). The partial geometry optimization was carried out in the same manner as described above, using the following restraints: $\nu_0 = -39.0^\circ$, $\nu_1 = 40.4^\circ$; $\nu_2 = -25.8^\circ$, $\nu_3 = 4.6^\circ$, $\nu_4 = 21.0^\circ$, $\chi = -81.9^\circ$, $\alpha = -61.4^\circ$, $\beta = -132.1^\circ$, $\gamma = 49.4^\circ$, $\delta = 129.8^\circ$. The pseudorotation phase (*P*) and amplitude (ψ_m) are 130˚ and 41˚, respectively.

All results presented below employ the GIAO method for calculating nuclear magnetic shielding tensors (Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789; Wolinski, K.;Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251). The following levels of theory were used: (i) restricted Hartree-Fock (RHF); (ii) DFT with the hybrid B3LYP functional (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648); (iii) DFT with the PBE exchange functional and PBE correlation functional (Perdew, J. P.; Burke, K.;Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865; Perdew; J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396). Slightly different results for C and G reflect not only the effect of the pyrimidine *vs* purine substituent at C1', but also the slightly different torsion angles in the ribose rings.

Table 1S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for C1'

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Cytidine	RHF/6-311+G*	15.8	1.5	-17.2
	B3LYP/6-311+G*	16.7	3.7	-20.4
	B3LYP/6-311++G**	16.5	4.0	-20.4
	B3LYP/cc-pVTZ	17.8	3.8	-21.6
	PBEPBE/cc-pVTZ	17.7	4.8	-22.5
Guanidine	RHF/6-311+G*	16.1	1.1	-17.2
	RHF/cc-pVTZ	16.4	1.4	-17.8
	B3LYP/6-311+G*	17.5	3.3	-20.8
	B3LYP/cc-pVTZ	17.7	3.7	-21.4
	PBEPBE/cc-pVTZ	17.7	4.2	-21.9

Table 2S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for C2'

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Cytidine	RHF/6-311+G*	11.1	6.5	-17.6
	B3LYP/6-311+G*	12.4	5.8	-18.2
	B3LYP/6-311++G**	12.0	6.0	-18.0
	B3LYP/cc-pVTZ	12.1	5.9	-18.0
	PBEPBE/cc-pVTZ	12.4	6.0	-18.4
Guanidine	RHF/6-311+G*	10.3	7.2	-17.5
	RHF/cc-pVTZ	10.8	6.6	-17.4
	B3LYP/6-311+G*	11.0	7.2	-18.2
	B3LYP/cc-pVTZ	11.2	6.5	-17.7
	PBEPBE/cc-pVTZ	11.8	6.5	-18.3

Table 3S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for C3'

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Cytidine	RHF/6-311+G*	28.2	6.9	-35.1
	B3LYP/6-311+G*	32.5	5.9	-38.4
	B3LYP/6-311++G**	32.4	6.0	-38.4
	B3LYP/cc-pVTZ	31.5	6.6	-38.1
	PBEPBE/cc-pVTZ	32.5	6.1	-38.5
Guanidine	RHF/6-311+G*	26.7	7.7	-34.4
	RHF/cc-pVTZ	26.2	8.4	-34.5
	B3LYP/6-311+G*	30.5	7.0	-37.5
	B3LYP/cc-pVTZ	29.4	7.5	-36.9
	PBEPBE/cc-pVTZ	30.4	7.4	-37.7

Table 4S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for C4'

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Cytidine	RHF/6-311+G*	28.5	6.5	-35.0
	B3LYP/6-311+G*	31.1	8.9	-40.0
	B3LYP/6-311++G**	30.9	8.9	-39.8
	B3LYP/cc-pVTZ	30.9	9.6	-40.5
	PBEPBE/cc-pVTZ	30.4	11.1	-41.5
Guanidine	RHF/6-311+G*	34.2	3.0	-37.2
	RHF/cc-pVTZ	34.2	3.7	-37.9
	B3LYP/6-311+G*	37.1	5.3	-42.4
	B3LYP/cc-pVTZ	37.4	5.5	-42.9
	PBEPBE/cc-pVTZ	36.5	7.6	-44.1

Table 5S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for C5'

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
Cytidine	RHF/6-311+G*	19.9	10.5	-30.4
	B3LYP/6-311+G*	24.8	13.4	-38.2
	B3LYP/6-311++G**	24.9	13.2	-38.1
	B3LYP/cc-pVTZ	24.7	13.0	-37.7
	PBEPBE/cc-pVTZ	26.1	13.7	-39.8
Guanidine	RHF/6-311+G*	21.3	10.4	-31.7
	RHF/cc-pVTZ	21.2	10.5	-31.6
	B3LYP/6-311+G*	27.0	12.8	-39.8
	B3LYP/cc-pVTZ	27.6	12.4	-40.0
	PBEPBE/cc-pVTZ	28.9	12.9	-41.8

Table 6S: Calculated Principal Components of the Traceless Anisotropic Chemical Shift Tensors for a C1'-exo Guanidine Nucleotide at the B3LYP/cc-pVTZ level.

	δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
C1'	32.2	3.2	-35.3
C2'	31.4	4.5	-35.9
C3'	25.1	3.8	-29.0
C4'	22.3	6.5	-28.8
C5'	15.5	13.7	-29.2

Table 7S: Direction Cosines Relating Typical Experimental (NMR structures) and Calculated Chemical Shift Tensor Principal Axis Systems[a]

Nucleus		δ_{11} (calc)	δ_{22} (calc)	δ_{33} (calc)
C1'	δ_{11} (expt)	0.8746	0.4848	0.0017
	δ_{22} (expt)	0.4726	0.8499	0.2317
	δ_{33} (expt)	0.1045	0.0017	0.9744
C2'	δ_{11} (expt)	0.4083	0.8965	0.1719
	δ_{22} (expt)	0.9100	0.3811	0.1357
	δ_{33} (expt)	0.0541	0.2130	0.9999
C3'	δ_{11} (expt)	0.9755	0.0958	0.1891
	δ_{22} (expt)	0.0924	0.9932	0.0872
	δ_{33} (expt)	0.1994	0.0610	0.9774
C4'	δ_{11} (expt)	0.8310	0.5105	0.2300
	δ_{22} (expt)	-0.5120	0.8581	0.0401
	δ_{33} (expt)	-0.1616	-0.1461	0.9763
C5'	δ_{11} (expt)[b]	-	-	0.143 ± 0.006
	δ_{22} (expt)	-	-	0.143 ± 0.006
	δ_{33} (expt)	0.0785	-0.1840	0.9796

[a] Experimental orientations are from a representative fit to the NMR-refined structure of Helix-35 RNA. Calculated orientations are from B3LYP/6-311+G* results for a guanidine nucleotide; however, the calculated orientations vary by a only a few degrees or less if different methods/basis sets are used.

[b] The experimental orientations of δ_{11} and δ_{22} for C5' are indeterminate due to the near-axial symmetry of the CS tensor.

Table 8S: Experimental average ribose carbon chemical shift tensor magnitudes and orientations (expressed as direction cosines)[c] determined for the A-form helical stem residues of Helix-35ψ RNA for the NMR-refined structures after adding random noise at the level of the experimental rmsd (Table 1, main text) to the experimental data, using a flat-bottom distribution. Results are the average of 50000 replicates over 10 experimental structures.

Nucleus		value / ppm	x[d]	y	z
C1'	δ_{11}	17.7 ± 1.4	0.002 ± 0.031	0.066 ± 0.019	-0.997 ± 0.001
	δ_{22}	-0.9 ± 0.5	0.977 ± 0.006	-0.210 ± 0.029	-0.013 ± 0.030
	δ_{33}	-16.8 ± 1.5	0.210 ± 0.030	0.975 ± 0.007	0.065 ± 0.020
C2'	δ_{11}	13.2 ± 3.0	-0.743 ± 0.072	-0.315 ± 0.102	0.564 ± 0.121
	δ_{22}	1.0 ± 1.1	-0.015 ± 0.141	-0.855 ± 0.066	-0.486 ± 0.098
	δ_{33}	-14.3 ± 2.5	0.646 ± 0.072	-0.386 ± 0.085	0.642 ± 0.099
C3'	δ_{11}	45.8 ± 2.4	0.571 ± 0.007	0.048 ± 0.043	-0.818 ± 0.006
	δ_{22}	4.1 ± 2.3	-0.029 ± 0.029	0.998 ± 0.002	0.038 ± 0.035
	δ_{33}	-49.9 ± 1.0	0.820 ± 0.005	0.002 ± 0.014	0.573 ± 0.007
C4'	δ_{11}	49.1 ± 9.0	0.055 ± 0.248	0.142 ± 0.153	0.942 ± 0.062
	δ_{22}	-1.8 ± 9.4	-0.852 ± 0.046	0.428 ± 0.081	-0.015 ± 0.286
	δ_{33}	-47.3 ± 3.0	0.452 ± 0.053	0.875 ± 0.030	-0.154 ± 0.055
C5'	δ_{11}	23.2 ± 4.0	0.628 ± 0.292	0.307 ± 0.189	0.130 ± 0.611
	δ_{22}	14.6 ± 3.3	-0.100 ± 0.527	-0.075 ± 0.321	0.702 ± 0.333
	δ_{33}	-37.8 ± 6.0	-0.473 ± 0.100	0.870 ± 0.057	0.056 ± 0.049

[c] The principal components are ordered $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, and refer to the traceless symmetric part of the chemical shift tensor.

[d] The xyz axis systems used are defined as follows. C1': x bisects the O4'-C1'-C2' angle, y is in the same plane, z is perpendicular to this plane (see Figure 1C); C2': x bisects the C1'-C2'-C3' angle, y is in the same plane, z is perpendicular to this plane; C3': x bisects the C2'-C3'-C4' angle, y is in the same plane, z is perpendicular to this plane; C4': x bisects the C3'-C4'-O4' angle, y is in the same plane, z is perpendicular to this plane; C5': x bisects the O5'-C5'-C4' angle, y is in the same plane, z is perpendicular to this plane.