Supporting Information

Experimental Acquisition Parameters: For measurements involving D5 and D6 a series of either 11 or 12 time points (typically 2 repeat points/data set) each comprised of 30 complex points in the indirect dimension (sweep width of 4500 Hz) recorded with 32 transients/FID were collected. Relaxation delays varied from 0.5-8.5 ms (R_1, 25 ^oC), 0.5-13.5 ms (R_1, 5 ^oC), 0.025-3 ms (R_2, 25^oC), 0.025-1.5 ms (R_2, 5^oC). The total acquisition time for each relaxation set was 12-14 hours. Rates for D1' were obtained from a series of data sets recorded with 34 complex points in the indirect dimension (3012 Hz, 64 transients/FID; 31 hours for each relaxation series comprised of 12 data sets). Relaxation delays between 0.5-10.5 ms (R_1, 25^oC), and 0.025-2.6 ms (R_2, 25^oC) were employed. Rates measured for D2' were based on data sets of 34 complex t_1 points (sweep width of 3012 Hz, 16 and 32 transients at 25 and 5^oC respectively, corresponding to measurement times of 8 and 16 hours for data at the two temperatures). Relaxation delays very similar to those used for D5/D6 were employed. Relaxation rates of D4' were obtained from 12 data sets (34 complex t_1 points, sweep width of 3000 Hz, 64 transients/FID, 32 hours per R_1,R_2 measurement). Relaxation delays between 0.5-7.5 ms (R_1, 25^oC), and 0.025-2.5 ms (R_2, 25^oC) were used. Relaxation delays varying from 0.5-10.5 ms (R_1, 25^oC), 0.5-13.5 ms (R_1, 5^oC), 0.025-3.0 ms (R_2, 25^oC) and 0.025-1.5 ms (R_2, 5^oC) were used for the measurement of rates for D5'/D5". 12 data sets comprised of 17 complex points in t_1 (sweep width 1500 Hz), 48 transients/FID were collected (11.5 hours per R_1,R_2 measurement).

Supporting Information Table 1: ^{2}H (R_1 and R_2) and ^{13}C (R_1) relaxation rates measured at various positions in the 14-mer RNA molecule at 25 and 5°C.

^{2}H 25°C						^{2}H 5°C						^{13}C 25°C				5°C	
Nucleus	Residue	$R_1(s^{-1})$	Error	$R_2(S^{-1})$	Error	Nucleus	Residue	$R_1(s^{-1})$	Error	$R_2(S^{-1})$	Error	Nucleus	Residue	$R_1(s^{-1})$	Error	$R_1(s^{-1})$	Error
D1'	G2	129.90	0.45	472.21	5.51	D2'	G2	78.57	0.33	793.49	7.01	C2'	G2	0.83	0.03	0.71	0.04
	C3	148.54	1.83	512.94	3.67		A4	80.58	0.59	818.22	3.52		A4	0.70	0.01	0.61	0.01
	A4	138.35	0.23	490.67	6.25		C5	85.25	0.52	783.29	9.89		C5	0.74	0.01	0.64	0.01
	C5	143.87	1.74	490.65	6.86		U6	86.75	0.19	753.94	7.72		U6	0.87	0.07	0.64	0.04
	U6	143.80	1.68	478.95	7.92		U7	73.02	0.70	721.99	6.13		U7	0.90	0.10	0.67	0.02
	U7	119.93	0.94	443.01	2.71		C8	76.28	1.94	745.85	8.93		C8	0.86	0.03	0.72	0.02
	C8	125.16	1.45	506.60	4.19		G9	85.94	0.68	781.96	7.40		G9	1.00	0.08	0.87	0.05
	G9	126.84	1.16	475.18	8.32		G12	78.92	0.60	828.88	8.89		G12	0.74	0.02	0.64	0.00
	G10	131.05	1.25	497.91	19.51		C13	81.57	0.25	806.39	6.18		C13	0.72	0.02	0.62	0.00
	U11	140.63	1.44	496.38	4.26		C14	100.70	0.63	615.39	5.04		C14	0.72	0.02	0.69	0.05
	G12	137.28	0.98	479.79	1.93	D5''	G1	95.09	1.01	622.07	15.61	C5'	G1	2.80	0.02	1.61	0.12
	C13	146.12	1.31	481.74	3.62		C3	89.33	0.45	717.94	11.54		G2	2.69	0.02	1.37	0.10
	C14	135.21	0.82	427.08	1.07		A4	87.71	1.28	747.28	20.05		C3	2.66	0.05	1.28	0.17
D2'	G2	133.09	0.86	515.54	6.34		U6	88.25	1.46	684.19	9.06		A4	2.67	0.05	1.33	0.17
	A4	136.49	1.22	527.78	7.21		U7	83.17	0.82	646.05	8.51		C5	2.69	0.01	1.35	0.16
	C5	141.78	0.43	512.55	5.19		C8	83.76	0.68	738.39	14.35		U6	2.83	0.02	1.36	0.11
	U6	143.63	1.31	499.53	2.01		G9	85.97	0.92	719.92	6.61		U7	2.64	0.03	1.38	0.12
	U7	122.80	0.90	465.23	5.06		G10	84.84	1.95	780.24	2.49		C8	2.64	0.02	1.33	0.12
	C8	129.01	0.12	474.75	1.57		U11	76.65	1.56	819.99	7.98		G9	2.67	0.03	1.34	0.14
	G9	137.03	0.29	505.36	4.73		G12	87.44	1.60	754.41	19.70		G10	2.74	0.02	1.43	0.13
	G12	133.93	1.47	533.41	8.03		C13	83.93	0.52	774.35	12.65		U11	2.73	0.01	1.35	0.19
	C13	135.51	1.30	531.09	1.60		C14	79.75	2.58	730.45	13.10		G12	2.64	0.03	1.27	0.18
	C14	128.19	0.62	367.85	1.67	D5'	G1	96.14	0.73	616.66	12.10		C13	2.55	0.04	1.33	0.16
D4'	G2	131.87	1.53	480.52	9.22		U6	75.50	0.29	826.14	13.19		C14	2.64	0.01	1.32	0.13
	C3	135.57	5.94	505.85	9.94		U7	82.77	0.57	735.25	14.05	C5	C3	1.64	0.02	1.15	0.05
	A4	136.12	2.98	460.07	3.48		C8	84.03	1.17	705.66	1.76		C5	1.59	0.02	1.22	0.05
	U7	126.70	0.57	485.37	7.69		G9	83.51	0.37	780.16	5.58		U6	1.47	0.01	1.17	0.06
	C8	134.31	0.51	458.59	4.17		G10	87.49	1.16	758.78	19.50		U7	1.13	0.02	0.88	0.02
	G9	134.40	0.92	472.40	9.31	D5	C3	106.61	1.66	840.45	37.04		C8	1.44	0.05	1.13	0.04
	G10	163.56	1.45	517.68	4.71		C5	107.39	6.15	889.91	12.82		U11	1.43	0.01	1.08	0.04
	U11	131.36	2.55	478.95	4.40		U6	101.40	1.42	850.76	23.91		C13	1.56	0.02	1.19	0.03
	G12	134.87	2.48	469.64	8.01		U7	88.42	1.28	737.40	11.97		C14	1.44	0.02	1.14	0.03
D5''	G1	134.93	0.39	397.19	1.78		C8	88.51	0.28	922.89	28.65	C6	C3	1.96	0.03	1.36	0.03
	G2	143.23	3.10	452.36	3.91		U11	104.84	3.01	912.45	20.82		C5	2.04	0.02	1.41	0.02
	C3	146.89	0.30	478.52	7.25		C13	104.15	0.75	910.36	10.80		U6	2.08	0.03	1.37	0.04
	A4	147.13	2.44	479.60	5.88		C14	96.60	2.33	878.65	20.60		U7	1.47	0.01	1.12	0.02
	U7	132.23	0.35	418.22	3.14	D6	C3	92.47	2.36	838.38	11.73		C8	1.82	0.02	1.23	0.03
	C8	134.35	1.11	466.13	2.57		C5	97.55	0.95	822.14	24.25		U11	2.11	0.01	1.42	0.03
	G9	139.90	0.90	461.38	4.43		U6	92.56	0.31	803.82	9.97		C13	2.01	0.02	1.37	0.01
	G10	139.81	1.13	494.81	7.08		U7	80.39	0.77	613.07	4.79		C14	1.98	0.04	1.35	0.02
	U11	130.34	1.44	514.13	4.58		C8	84.76	2.68	829.66	7.31						
	G12	144.97	1.52	476.73	8.92		U11	92.89	1.76	808.43	33.02						
D5'	G1	130.74	1.11	362.40	1.25		C13	89.72	0.84	805.13	13.55						
	G2	134.04	3.00	462.40	5.71		C14	92.78	3.34	788.15	12.35						
	U6	126.21	1.41	507.99	2.61												
	U7	137.27	3.49	468.19	5.13												
	C8	135.27	0.60	460.68	1.27												
	G9	135.78	1.94	493.79	1.99												
	G10	140.72	1.17	480.30	5.16												
D5	C3	168.18	0.98	573.36	2.66												
	C5	166.26	4.62	585.85	8.83												
	U6	169.03	4.44	572.53	9.09												
	U7	134.48	1.21	467.65	5.26												
	C8	156.04	2.53	558.94	5.24												
	U11	168.45	1.99	576.37	8.18												
	C13	175.33	2.71	606.05	20.80												
	C14	161.69	2.88	572.69	3.64												
D6	C3	154.91	2.55	541.18	3.13												
	C5	157.49	1.13	537.07	9.78												
	U6	150.99	0.98	520.89	1.94												
	U7	118.42	0.97	395.24	2.96												
	C8	141.42	1.03	530.67	3.46												
	U11	152.14	1.48	532.84	0.14												
	C13	150.53	0.45	556.72	4.31												
	C14	152.13	1.03	516.93	9.38												

Supporting Information Table 2: S^2 and τ^f for the 14-mer from analysis of ^2H relaxation rates at 25 and 5°C.

25°C						5°C					
Nucleus	Residue	S^2	Error	τ^f(ps)	Error	Nucleus	Residue	S^2	Error	τ^f(ps)	Error
D1'	2	0.817	0.015	21.4	28.7	D2'	2	0.883	0.012	1.1	5.5
	3	0.908	0.018	44.9	65.1		4	0.906	0.014	16.6	22.8
	4	0.862	0.012	2.8	14.6		5	0.909	0.014	4.9	15.0
	5	0.874	0.016	23.2	41.7		6	0.895	0.013	7.1	19.2
	6	0.853	0.021	60.5	60.3		7	0.805	0.016	14.4	18.9
	7	0.763	0.013	6.6	16.9		8	0.845	0.015	2.9	9.3
	8	0.840	0.012	1.9	9.9		9	0.909	0.014	12.2	26.2
	9	0.803	0.019	46.3	41.5		12	0.896	0.016	47.6	28.7
	10	0.838	0.025	24.9	39.9		13	0.904	0.015	14.2	23.2
	11	0.860	0.021	72.7	62.0		14	0.681	0.018	284.8	19.5
	12	0.849	0.013	7.5	19.6	D5''	1	0.704	0.022	219.5	18.9
	13	0.856	0.023	88.7	67.0		3	0.856	0.019	83.4	32.9
	14	0.746	0.023	114.4	43.8		4	0.882	0.023	44.5	37.9
D2'	2	0.872	0.015	13.3	28.4		6	0.738	0.020	203.4	20.7
	4	0.895	0.013	4.3	17.7		7	0.724	0.018	133.2	18.5
	5	0.893	0.013	1.3	9.9		8	0.837	0.021	87.5	36.4
	6	0.884	0.015	17.5	39.7		9	0.843	0.020	74.0	35.4
	7	0.794	0.013	2.8	11.2		10	0.897	0.015	24.8	30.0
	8	0.819	0.014	8.2	20.2		11	0.865	0.013	0.0	0.0
	9	0.870	0.012	0.3	5.2		12	0.893	0.018	17.1	28.0
	12	0.885	0.018	57.2	51.1		13	0.893	0.013	0.4	3.1
	13	0.895	0.016	12.6	29.9		14	0.834	0.020	38.8	35.8
	14	0.585	0.021	210.0	26.6	D5'	1	0.682	0.018	240.3	17.5
D4'	2	0.820	0.020	58.2	44.8		6	0.862	0.012	0.0	0.0
	3	0.885	0.016	7.8	30.2		7	0.856	0.016	23.3	26.7
	4	0.821	0.017	26.2	36.8		8	0.842	0.016	20.2	24.4
	7	0.817	0.012	0.0	0.0		9	0.890	0.017	23.7	32.2
	8	0.816	0.015	16.2	28.7		10	0.824	0.028	193.8	31.4
	9	0.832	0.013	5.5	17.4	D5	3	0.861	0.042	114.4	51.4
	10	0.788	0.031	954.8	340.8		5	0.883	0.023	198.5	129.8
	11	0.829	0.014	14.2	26.2		6	0.865	0.026	66.6	45.1
	12	0.829	0.015	13.9	28.0		7	0.745	0.018	43.3	20.2
D5''	1	0.665	0.022	176.6	31.0		8	0.839	0.015	0.0	0.0
	2	0.791	0.022	129.1	54.4		11	0.935	0.018	16.0	39.7
	3	0.846	0.023	90.6	65.0		13	0.883	0.023	179.1	49.9
	4	0.838	0.024	128.8	68.2		14	0.858	0.023	69.1	42.7
	7	0.667	0.023	204.0	32.9	D6	3	0.923	0.015	9.7	24.4
	8	0.808	0.021	47.1	48.3		5	0.923	0.023	42.3	50.7
	9	0.806	0.023	86.4	56.9		6	0.896	0.015	22.1	32.0
	10	0.863	0.013	13.1	26.8		7	0.665	0.017	85.6	14.2
	11	0.841	0.012	0.0	0.0		8	0.871	0.019	41.4	43.0
	12	0.843	0.021	71.7	60.0		11	0.893	0.029	36.0	42.0
D5'	1	0.562	0.021	225.1	23.6		13	0.889	0.013	2.1	8.6
	2	0.761	0.025	154.3	52.3		14	0.891	0.018	27.0	41.3
	6	0.821	0.012	0.0	0.0						
	7	0.815	0.021	60.3	54.5						
	8	0.812	0.016	25.1	34.5						
	9	0.843	0.018	38.4	45.0						
	10	0.792	0.026	196.9	58.4						
D5	3	0.875	0.019	34.0	50.8						
	5	0.866	0.024	113.8	91.0						
	6	0.868	0.023	81.2	80.5						
	7	0.710	0.014	10.6	17.2						
	8	0.826	0.022	60.4	54.5						
	11	0.882	0.016	25.5	43.0						
	13	0.883	0.039	269.5	123.1						
	14	0.828	0.026	149.8	66.6						
D6	3	0.887	0.023	94.7	77.1						
	5	0.901	0.017	25.4	50.2						
	6	0.861	0.021	55.7	58.9						
	7	0.634	0.020	65.5	25.4						
	8	0.841	0.022	67.7	59.7						
	11	0.883	0.015	20.3	42.3						
	13	0.903	0.012	1.4	10.6						
	14	0.866	0.017	29.6	46.6						