Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

DNA and RNA sugar-phosphate backbone emerges as the key player. Overview of quantum-chemical, structural biology and simulation studies.

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Mathematical relation between the individual torsions of ribose and deoxyribose rings, the sugar pucker phase and amplitude. This particular definition is valid for five membered rings and is specifically used for nucleic acids.

ν_0 - C4'-O4'-C1'-C2'

ν_1 - O4'-C1'-C2'-C3'

ν_2 - C1'-C2'-C3'-C4'

ν_3 - C2'-C3'-C4'-O4'

ν_4 - C3'-C4'-O4'-C1'

$$P = \arctan\left(\frac{(\nu_4 + \nu_1) - (\nu_3 + \nu_0)}{2 \times \nu_2 \times (\sin 36° + \sin[72°])}\right)$$

The pseudorotation P can take a value between 0° and 360°. If ν_2 is negative, then 180° is added to the value of P.

$$\tau_m = \frac{\nu_2}{\cos P}$$

Figure S1 Sugar conformations typical of B-DNA (C2'-endo, left) and A-RNA (C3'-endo, right). The plane defined by C4'-O4'-C1' atoms is perpendicular to the picture plane.

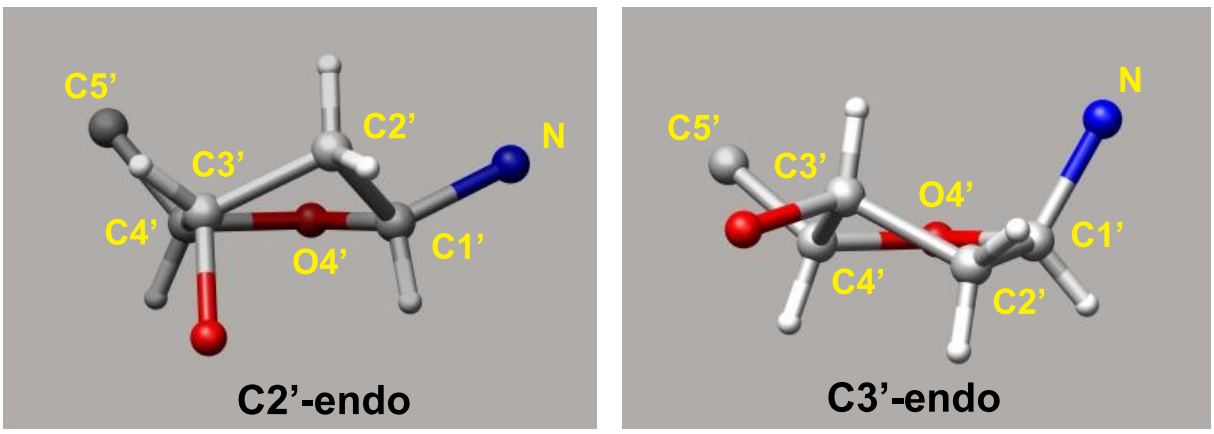

Figure S2 Histograms for the torsion angles (°) for A-DNA, B-DNA, and A-DNA+B-DNA. Histograms were generated for structures with resolution of 1.9 Å or better. Noncanonical DNA structures (quadruplex DNA, Z-DNA etc.) are not included.

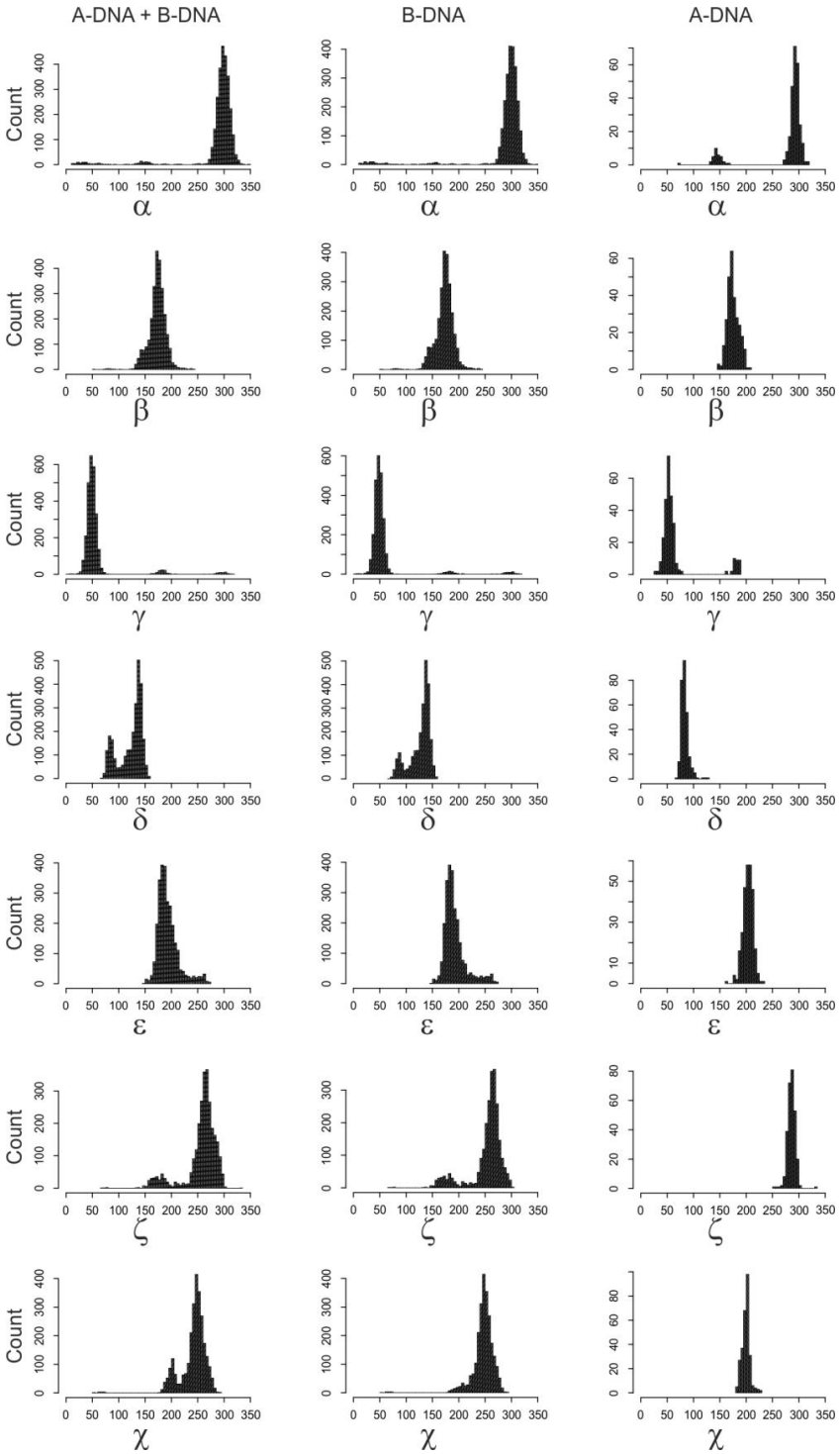

Figure S3 QM/MM hybrid computations can be used to qualitative assessment of different pathways of the sugar-phosphate self-cleavage in small ribozymes. The Figure shows several pathways of the selfcleavage investigated for the Hairpin ribozyme. Namely, thepathway, in which deprotonated guanine G8- and protonated adenine A38H+ act as a general base and a general acid, respectively (left pannels and upper free energy profile), and mechanism, where proton of 2‘-OH hydroxyl is shuttled through non-bridging oxygen into leaving O5‘ alcoholate (right pannels and lower free energy profile).

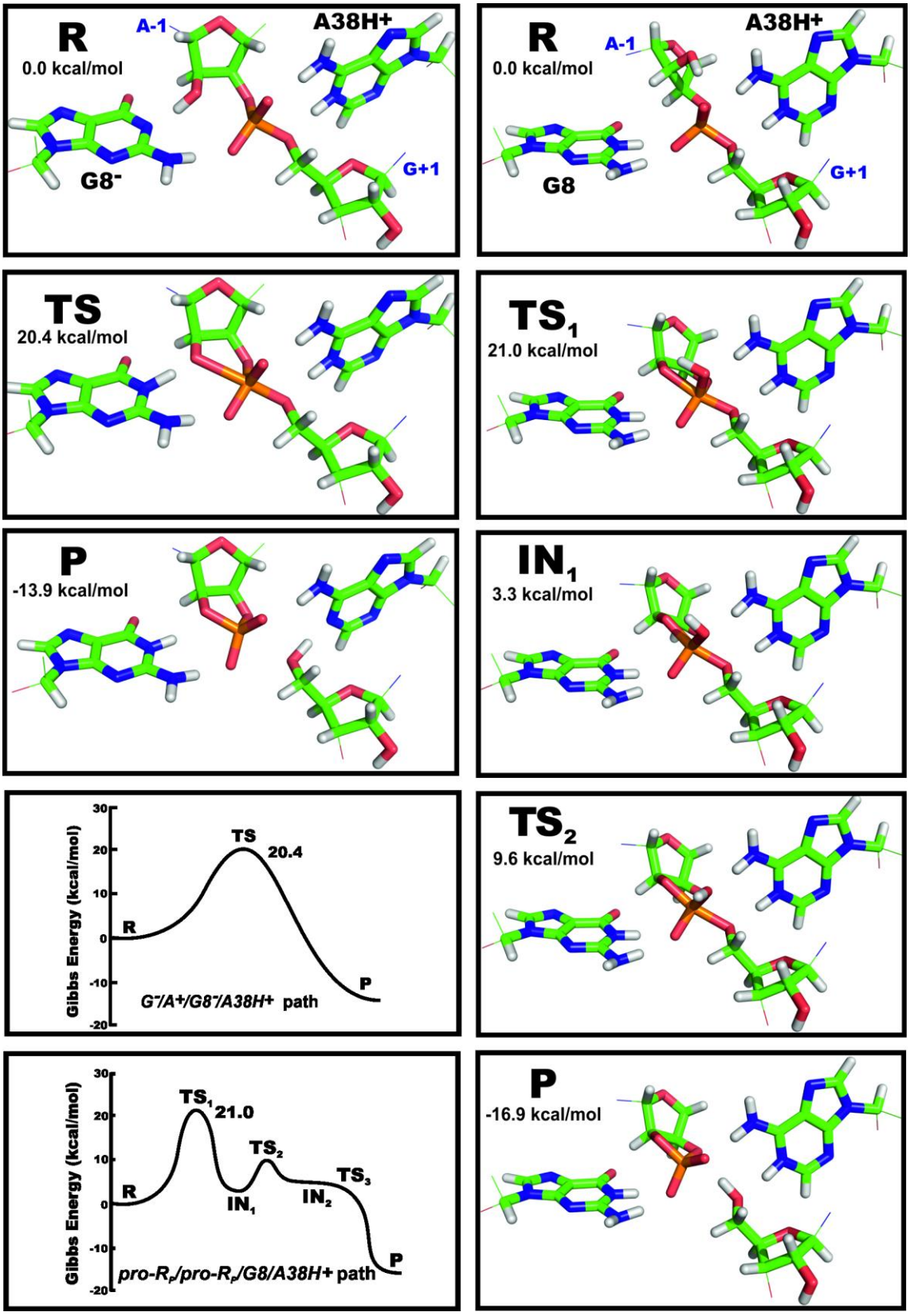

Table S1 Relative energies of the canonical α/γ g-/g+ (a1-a11) and noncanonical g+/t (b1-b9, q1-3) MP2/6-31+G* optimized conformers calculated by density functional-based methods, SPSOM model, gas phase. Reference CBS(T) is an alternative abbreviation for estimated CCSD(T)/CBS calculations [1].

α/γ	System	B3LYP[¶]	PBE-DG [°]	TPSS-D [◊]	mPW2-PLYP[°]	M06[¶]	M06L[¶]	M06HF[¶]	M062X[¶]	CBS(T)
g-/g+	a1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	a2	-0.99	-0.56	-0.81	-0.85	-1.08	-0.79	-1.16	-0.79	-0.76
	a3	2.30	2.08	2.19	2.53	2.56	2.40	2.83	2.60	2.61
	a4	-0.07	-0.18	-0.32	-0.18	-0.68	-0.17	-0.42	-0.25	-0.34
	a5	-0.32	0.04	0.07	-0.09	0.15	0.28	0.13	0.14	0.14
	a6	1.03	0.95	0.87	1.19	1.10	1.15	1.23	1.27	1.16
	a7	0.00	0.17	0.23	0.01	0.06	0.23	0.14	0.16	0.17
	a8	-0.43	0.63	0.67	0.25	0.51	0.87	0.62	0.95	0.66
	a9	0.07	0.13	0.17	0.00	-0.17	0.21	-0.21	-0.01	-0.03
	a10	2.58	1.51	1.86	2.27	2.24	2.31	2.45	2.19	2.19
	a11	-0.49	0.15	-0.11	-0.15	-0.30	0.18	-0.12	0.24	0.02
	RSoS/N[†]	**0.209**	**0.091**	**0.044**	**0.032**	**0.038**	**0.024**	**0.034**	**0.015**	**0.000**
g+/t[‡]	b1	6.00	7.52	7.15	6.78	7.86	8.64	8.45	8.62	7.58
	b2	6.25	7.88	7.80	7.29	8.85	9.46	8.97	9.15	8.25
	b3	5.73	7.68	7.10	6.76	7.99	8.88	8.81	8.84	7.82
	b4	5.35	6.98	6.91	6.27	7.55	8.24	7.92	8.02	7.23
	b5	6.72	7.90	7.45	7.29	8.37	9.15	8.98	9.15	7.93
	b6	6.46	8.17	7.70	7.45	8.61	9.33	9.01	9.28	8.25
	b7	6.08	7.42	7.11	6.92	8.24	8.75	8.95	8.86	7.74
	b8	5.40	7.12	6.77	6.23	7.34	8.21	7.97	8.01	7.10
	RSoS/N	**3.089**	**0.042**	**0.256**	**0.761**	**0.150**	**1.205**	**0.829**	**1.023**	**0.000**

g+/t[§]	q1	1.80	1.84	1.98	1.98	1.24	2.28	2.24	2.44	1.87
	q2	2.36	2.10	2.30	2.37	1.58	2.68	2.53	2.63	1.94
	q3	2.03	1.49	1.81	2.29	1.98	2.72	2.95	2.77	1.81
	RSoS/N	**0.077**	**0.043**	**0.047**	**0.142**	**0.185**	**0.515**	**0.595**	**0.574**	**0.000**

[†] RSoS/N is the sum of squares (RSoS) divided by the number of conformers (N_r; N_a=10, N_b=8, N_q=3, a1 excluding) belonging to the respective conformational region (a, b, q) defined as $\frac{1}{N_r}\sum_{i,region}\left(E_i^{Method}-E_i^{CBS(T)}\right)^2$

[‡] Pathological g+/t conformers emerging in long MD "AMBER"simulations prior parmbsc0 correction.

[§] Real g+/t conformers from parallel stranded human telomeric guanine quadruplex loops.

[¶]: 6-31+G* basis set; [°]: TZVPP basis set; [◊]: 6-311++G(3df, 3pd) basis set

1. A. Mladek, J. E. Sponer, P. Jurecka, P. Banas, M. Otyepka, D. Svozil and J. Sponer, *J. Chem. Theory Comput.*, 2010, 6, 3817-3835.