Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION

Nucleotides containing variously modified sugars: energetics, structure, and mechanical properties

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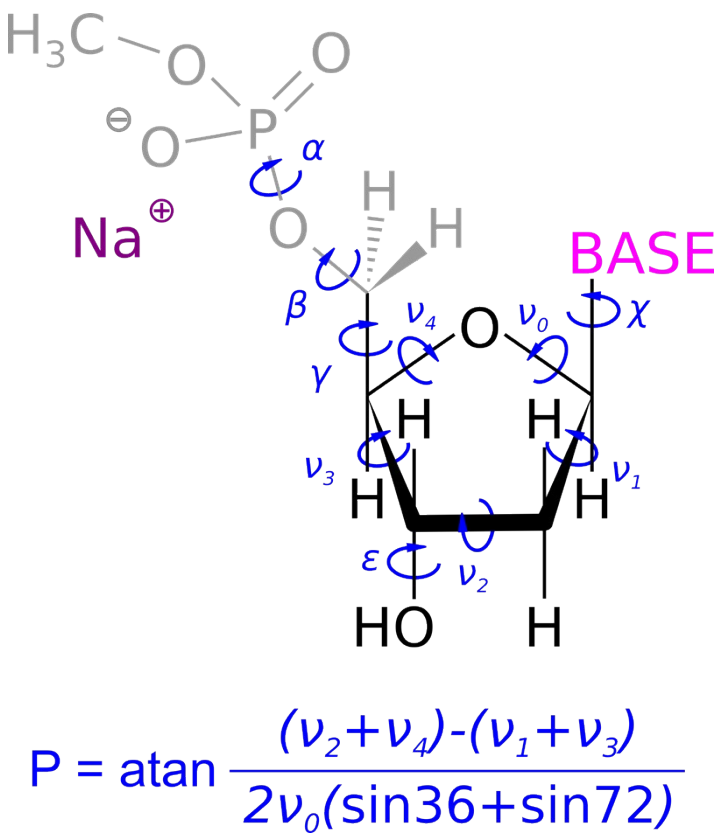

Figure S1. The definition of the pseudorotational phase angle *P*, which is calculated based on endocyclic torsion angles $\nu_0 \div \nu_4$ inside the ribose sugar ring.

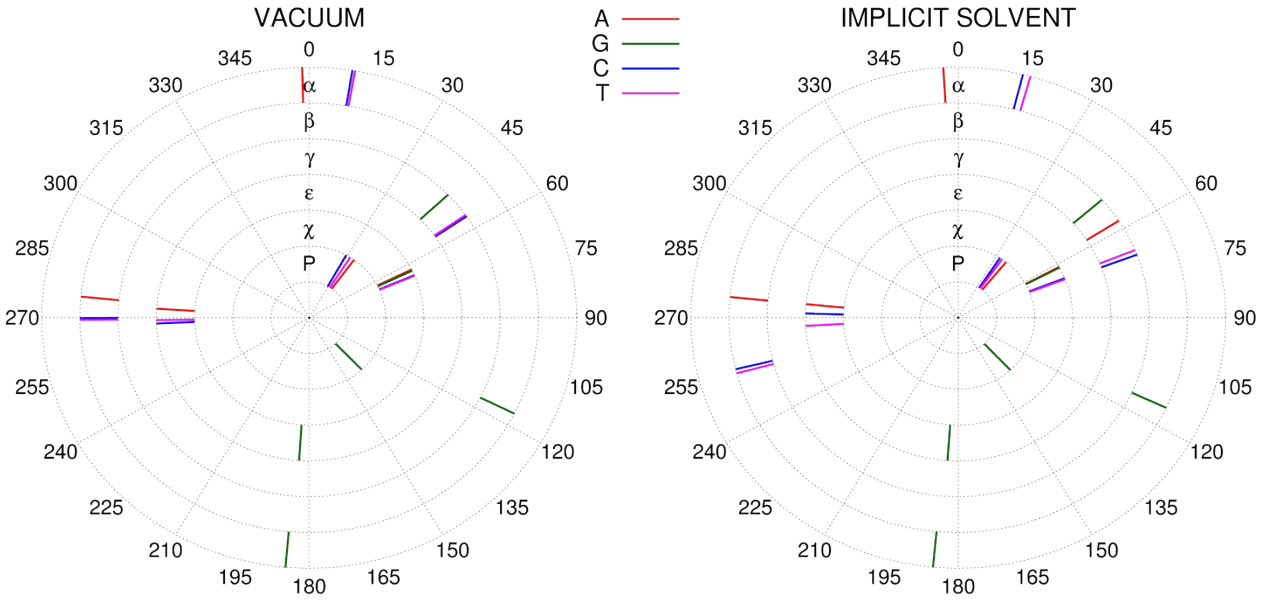

Figure S2. Polar plots showing the geometrical parameters of the most stable conformers of canonical nucleotides with A, G, C, and T nucleobases. The geometries were optimized in vacuum (left) or using the IEFPCM solvent model (right). The level of optimization was B3LYP/6-31G(d,p) in both cases. The geometries were taken from Ref. 64. The methodology of conformational analysis that allows identifying a full conformational set (all possible conformers of nucleotides) and therefore locating the most stable conformers is also described in Ref. 64.

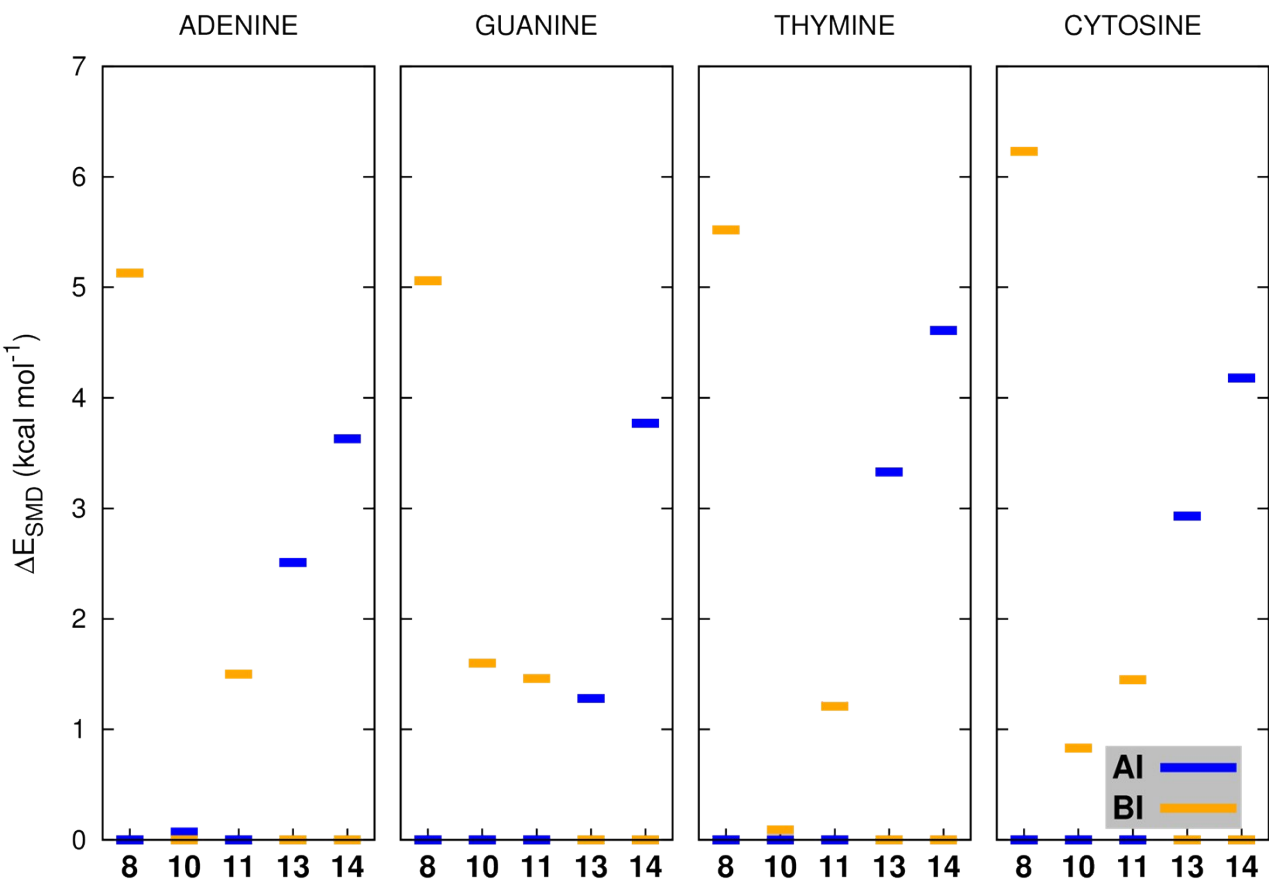

Figure S3. Relative electronic energies (in kcal/mol) in water estimated by SMD model (ref. 95 in the manuscript) for dNs with selected sugar modifications (**8**, **10**, **11**, **13**, and **14**) including four canonical nucleobases.

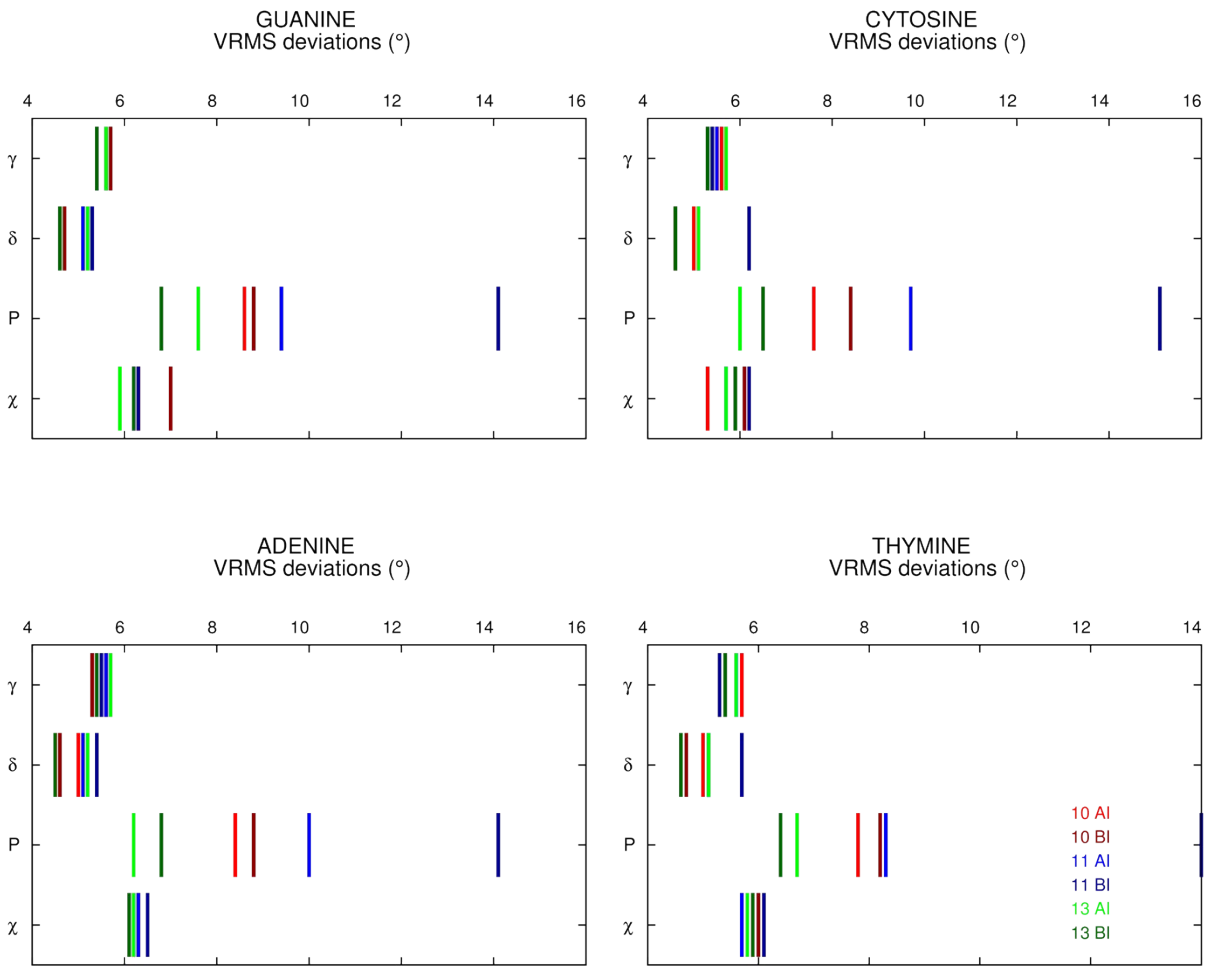

Figure S4. The scale of vibrational root-mean-square (VRMS) deviations at T = 0K for dNs with the sugar residues **10**, **11** and **13**

Table S1. The energetic and conformational characteristics of 2′-deoxyribonucleotide-5′-monophosphates (dNs) with variously modified sugar residues. For each structural parameter the values of calculated relaxed force constants are shown. The RFC unit is kcal mol^{-1} rad^{-2} for conformational angles (α, β, γ, δ, χ, and P) and N m^{-1} for glycosidic bond lengths l_{glycos}. The geometry optimization followed by vibrational calculations was performed at the B3LYP-D3/6-311++G(d,p) level of theory in the Gaussian 09 package using the *tight* convergence criteria and *ultrafine* integration grid options.

				Conformational parameters[a]													Energetic features[b]		
				A		β		γ		δ		χ		P		l_{glycos}		ΔE_{VAC}	ΔG_{VAC}	ΔE_{CPCM}
				Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC			
UNS	**1**	dA	DNA	-56.5	15.6	155.0	15.7	50.9	33.5	-	-	-103.1	10.0	27.4	0.0	1.456	398.4	-	-	-
		dC	DNA	-49.9	18.2	150.6	18.8	53.1	36.3	-	-	-112.7	5.4	73.0	0.3	1.467	374.5	-	-	-
		dG	DNA	-56.8	13.9	155.1	13.0	49.9	31.6	-	-	-99.5	10.1	261.7	0.0	1.457	396.8	-	-	-
		dT	DNA	-58.5	21.5	159.1	13.7	51.2	32.2	-	-	-115.9	9.3	86.5	1.1	1.466	380.2	-	-	-
	2	dA	DNA	-56.5	14.6	155.6	15.0	51.2	35.7	-	-	-104.7	8.5	244.1	0.0	1.450	414.9	-	-	-
		dC	DNA	-51.1	16.8	151.9	18.6	52.5	36.1	-	-	-108.4	7.6	75.1	0.1	1.459	392.2	-	-	-
		dG	DNA	-56.7	13.9	156.0	11.8	50.3	32.9	-	-	-102.2	8.8	243.1	0.0	1.450	413.2	-	-	-
		dT	DNA	-59.0	21.9	160.2	11.6	50.9	31.7	-	-	-115.3	11.2	88.1	0.8	1.459	396.8	-	-	-
	3	dA	DNA	-57.7	15.1	155.6	13.5	50.9	36.2	-	-	-102.0	9.2	184.1	0.0	1.452	408.2	-	-	-
		dC	DNA	-51.2	16.5	150.8	18.7	53.0	37.6	-	-	-110.1	6.7	81.1	0.2	1.461	386.1	-	-	-
		dG	DNA	-58.4	13.1	156.3	10.9	49.7	29.2	-	-	-98.0	8.3	239.4	0.0	1.452	404.9	-	-	-
		dT	DNA	-60.0	20.6	160.3	9.5	51.1	30.2	-	-	-114.3	9.5	91.7	1.0	1.462	389.1	-	-	-
	4	dA	DNA	-70.6	12.8	175.3	12.0	48.7	33.3	-	-	-95.2	10.8	260.3	2.3	1.454	450.5	-	-	-
		dC	DNA	-66.9	12.5	173.0	13.1	49.9	35.6	-	-	-90.3	11.9	264.4	3.0	1.465	420.2	-	-	-
		dG	DNA	-71.6	13.3	174.1	11.5	48.2	33.8	-	-	-90.5	13.1	259.7	2.9	1.454	450.5	-	-	-
		dT	DNA	-68.0	18.0	176.0	14.5	48.0	35.4	-	-	-106.9	10.3	253.3	0.7	1.464	429.2	-	-	-
	5	dA	DNA	-75.8	11.1	165.7	4.4	55.1	31.0	-	-	-94.3	4.5	259.9	1.2	1.470	406.5	-	-	-
		dC	DNA	-73.4	15.2	165.4	10.1	55.3	32.0	-	-	-79.8	20.6	264.4	3.2	1.483	377.4	-	-	-
		dG	DNA	-76.2	11.9	161.5	4.8	55.1	27.9	-	-	-91.4	8.1	260.2	1.2	1.471	406.5	-	-	-
		dT	DNA	-72.4	14.4	170.5	6.8	55.8	30.8	-	-	-114.5	8.0	127.3	0.04	1.481	386.1	-	-	-
	6	dA	AI	-72.0	11.9	161.7	7.5	58.4	31.3	80.6	32.4	-145.5	7.5	359.4	25.8	1.470	409.8	2.22	1.13	1.62
			BI	-58.4	14.0	165.5	14.6	59.7	36.2	150.4	45.1	-104.2	8.2	182.0	19.3	1.461	434.8	0.00	0.00	0.00
		dC	AI	-66.8	12.6	164.6	8.6	59.7	32.2	80.7	39.6	-156.2	9.9	357.3	31.6	1.484	377.4	1.20	1.09	1.49
			BI	-55.2	13.7	167.1	13.5	62.2	33.6	148.3	45.2	-119.3	6.7	178.4	24.3	1.469	413.2	0.00	0.00	0.00
		dG	AI	-72.7	11.1	160.1	7.9	58.1	31.3	80.5	34.5	-144.7	7.0	0.7	27.7	1.470	408.2	2.66	1.51	1.69
			BI	-58.4	14.0	164.2	15.3	59.0	33.0	150.4	42.2	-102.4	8.5	181.3	21.6	1.460	434.8	0.00	0.00	0.00
		dT	AI	-71.6	16.7	162.3	10.6	58.6	36.3	80.6	42.7	-147.4	9.0	2.1	30.1	1.483	380.2	1.83	1.36	1.87
			BI	-57.3	17.2	168.4	13.8	61.9	35.1	148.0	43.7	-119.2	9.7	176.3	28.3	1.469	420.2	0.00	0.00	0.00

				Conformational parameters[a]														Energetic features[b]		
				α		β		γ		δ		χ		P		l_{glycos}		ΔE_{VAC}	ΔG_{VAC}	ΔE_{CPCM}
				Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC			
LOC	**7**	dA	AI	-58.6	11.6	151.3	12.6	54.8	26.6	67.1	69.2	-161.9	8.5	14.4	66.5	1.460	409.8	-	-	-
		dC	AI	-55.4	10.3	150.8	11.2	56.3	33.1	67.3	69.8	-168.2	23.6	14.6	67.4	1.478	375.9	-	-	-
		dG	AI	-58.2	10.3	150.6	12.3	54.2	28.7	67.3	60.4	-161.1	9.3	14.7	58.4	1.460	409.8	-	-	-
		dT	AI	-54.9	15.4	150.6	14.5	55.3	32.1	67.8	73.2	-165.0	15.3	14.3	67.2	1.484	369.0	-	-	-
HET	**8**	dA	AI	-56.4	12.7	153.6	11.9	50.8	33.1	-	-	-138.4	5.9	11.6	15.4	1.462	395.3	0.00	0.00	0.00
			BI	-46.8	11.6	152.8	12.0	56.1	36.6	-	-	-103.8	10.1	170.4	9.4	1.444	446.4	3.85	4.51	4.41
		dC	AI	-51.1	13.4	153.7	11.7	54.9	32.5	-	-	-159.2	11.5	12.0	22.2	1.481	363.6	0.00	0.00	0.00
			BI	-44.9	16.7	151.5	15.3	59.9	36.2	-	-	-117.7	8.9	162.8	10.1	1.454	421.9	6.00	5.69	4.10
		dG	AI	-56.1	11.5	152.9	12.2	49.6	30.4	-	-	-134.8	4.8	11.8	16.6	1.462	395.3	0.00	0.00	0.00
			BI	-46.2	10.5	152.3	10.0	55.1	34.1	-	-	-101.1	10.2	171.1	8.8	1.444	444.4	3.42	4.18	4.44
		dT	AI	-58.7	19.8	158.2	13.1	52.2	28.6	-	-	-147.8	7.6	17.7	18.5	1.480	353.4	0.00	0.00	0.00
			BI	-49.6	17.6	157.3	12.1	58.1	39.6	-	-	-115.9	11.2	161.1	10.8	1.454	425.5	4.76	4.90	5.02
	9	dA	AI	-61.1	14.4	151.1	15.3	55.8	30.5	-	-	-136.5	4.5	11.0	9.0	1.458	411.5	1.82	0.56	0.18
			BI	-48.2	11.8	154.9	9.6	63.4	43.9	-	-	-102.6	10.4	168.6	9.2	1.445	444.4	0.00	0.00	0.00
		dC	AI	-54.5	15.1	151.1	14.9	58.3	32.3	-	-	-155.6	17.2	5.2	20.0	1.475	381.7	0.00	0.00	0.00
			BI	-46.0	17.9	153.1	13.3	66.8	40.4	-	-	-117.4	8.1	159.7	11.2	1.454	420.2	1.17	1.02	1.13
		dG	AI	-61.8	13.4	150.4	13.3	54.8	30.0	-	-	-129.9	1.2	0.1	3.4	1.458	406.5	2.74	1.10	0.37
			BI	-48.4	10.3	155.3	7.3	62.6	41.0	-	-	-99.6	10.1	170.1	8.3	1.445	442.5	0.00	0.00	0.00
		dT	AI	-60.7	20.2	154.8	13.4	57.3	29.0	-	-	-151.1	9.2	9.4	19.9	1.478	370.4	0.37	0.00	0.00
			BI	-50.0	16.4	158.9	8.3	65.1	41.4	-	-	-114.5	10.3	159.5	12.3	1.455	423.7	0.00	0.34	0.34
FLR	**10**	dA	AI	-57.3	12.0	152.7	14.8	52.6	33.5	82.5	44.2	-140.1	5.9	11.5	16.6	1.457	408.2	3.65	2.22	1.15
			BI	-43.7	10.3	151.9	9.9	55.1	38.3	147.8	44.6	-102.6	10.7	167.0	10.3	1.441	454.5	0.00	0.00	0.00
		dC	AI	-51.6	12.9	152.3	13.6	55.9	33.6	79.9	53.6	-159.4	14.8	10.4	23.9	1.477	374.5	0.86	0.00	0.00
			BI	-43.7	16.7	152.3	15.6	58.3	38.1	145.6	42.1	-110.2	11.5	163.2	14.8	1.449	432.9	0.00	0.11	0.04
		dG	AI	-56.6	11.4	151.8	13.1	51.8	29.2	83.1	41.7	-138.3	5.6	12.1	13.8	1.457	408.2	1.31	2.10	0.00
			BI	-69.7	6.9	153.2	6.6	42.2	23.4	146.7	36.4	-126.1	4.8	164.4	7.5	1.442	450.5	0.00	0.00	0.57
		dT	AI	-59.5	18.8	156.8	13.7	54.1	31.1	79.8	47.6	-150.4	7.9	16.2	22.0	1.476	363.6	2.56	1.29	0.65
			BI	-46.9	15.6	156.8	11.2	57.1	39.5	145.6	42.5	-111.1	13.7	161.8	16.3	1.450	436.7	0.00	0.00	0.00
	11	dA	AI	-58.3	13.1	152.3	14.9	51.5	34.4	87.6	27.9	-131.5	5.0	6.2	9.5	1.450	420.2	0.00	0.00	0.00
			BI	-39.7	2.7	146.7	3.2	57.2	24.4	131.8	13.3	-113.6	7.6	148.5	1.7	1.438	465.1	1.66	2.11	1.41
		dC	AI	-51.6	13.5	150.1	14.6	53.5	38.9	86.7	38.3	-140.9	10.6	14.5	10.3	1.461	396.8	0.00	0.00	0.00
			BI	-42.4	11.5	149.7	11.7	61.1	27.9	124.7	5.6	-130.3	9.4	136.5	1.3	1.449	438.6	1.89	1.42	1.39
		dG	AI	-58.0	11.3	152.1	12.8	51.1	30.6	87.0	33.0	-133.1	5.1	6.8	9.7	1.450	418.4	0.00	0.00	0.00
			BI	-41.8	4.3	148.8	4.0	56.9	30.3	133.5	15.6	-109.9	9.2	152.9	2.3	1.439	463.0	1.78	2.30	1.55
		dT	AI	-59.3	18.9	155.3	15.0	52.8	34.2	85.3	41.6	-141.2	11.2	19.7	11.5	1.462	376.8	0.00	0.00	0.00
			BI	-48.3	13.1	155.3	11.5	59.6	35.8	123.3	9.5	-125.5	12.2	132.3	2.1	1.450	458.2	1.92	2.04	1.31

				Conformational parameters[a]														Energetic features[b]		
				α		β		γ		δ		χ		P		l_{glycos}		ΔE_{VAC}	ΔG_{VAC}	ΔE_{CPCM}
				Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC	Value	RFC			
FLR	**12**	dA	AI	-57.2	12.9	152.7	15.1	51.8	36.4	85.8	39.2	-134.8	7.4	10.6	10.1	1.445	438.6	0.00	0.00	0.00
			BI	-41.8	5.3	149.2	6.1	58.1	30.2	135.7	22.2	-112.1	10.5	156.2	3.2	1.435	471.7	0.17	1.09	1.13
		dC	AI	-51.3	14.1	150.3	15.0	53.4	40.5	85.1	43.2	-141.3	10.0	14.6	13.3	1.457	404.9	0.00	0.00	0.00
			BI	-43.3	13.8	151.3	13.7	61.9	35.5	132.6	19.8	-122.0	12.9	151.6	4.6	1.444	448.4	0.95	1.37	1.40
		dG	AI	-56.5	11.4	152.3	14.2	51.5	37.1	85.4	39.7	-136.6	7.0	11.1	12.1	1.446	436.7	0.00	0.00	0.00
			BI	-43.3	7.4	151.4	7.8	57.6	33.8	136.6	26.0	-110.4	10.8	158.9	3.5	1.435	469.5	0.30	1.47	1.21
		dT	AI	-59.2	19.7	155.7	14.7	52.6	34.3	84.2	43.4	-140.5	10.9	20.4	12.9	1.457	408.2	0.00	0.00	0.00
			BI	-73.3	11.7	-90.9	15.6	81.5	17.1	96.1	18.2	53.5	24.1	95.7	11.4	1.458	452.5	0.79	1.29	1.27
	13	dA	AI	-70.8	8.2	174.8	9.7	50.1	22.1	85.1	37.1	-135.1	3.7	346.1	26.4	1.457	446.4	2.44	1.17	2.81
			BI	-60.6	12.6	175.8	12.9	55.7	39.7	151.2	49.2	-99.8	9.4	192.1	20.9	1.449	469.5	0.00	0.00	0.00
		dC	AI	-64.2	11.5	174.4	11.4	52.2	28.7	84.8	37.9	-145.6	7.6	345.3	42.0	1.468	416.7	1.73	1.04	3.16
			BI	-55.3	11.0	176.5	13.7	57.2	41.7	149.5	46.9	-114.3	10.5	188.2	31.0	1.458	444.4	0.00	0.00	0.00
		dG	AI	-79.3	12.9	169.7	12.9	49.2	35.4	100.3	24.8	-94.0	13.5	327.1	13.6	1.455	452.5	2.81	2.48	2.25
			BI	-62.2	12.1	174.4	14.4	54.6	40.9	151.5	45.5	-93.8	9.1	193.6	19.3	1.450	467.3	0.00	0.00	0.00
		dT	AI	-71.5	14.4	173.9	13.6	49.7	38.5	85.8	38.4	-134.4	8.1	348.6	27.4	1.467	423.7	2.55	1.75	3.27
			BI	-57.2	19.1	176.5	15.0	56.4	42.5	149.6	47.7	-111.0	12.3	187.3	33.5	1.460	448.4	0.00	0.00	0.00
	14	dA	AI	-69.1	7.9	177.2	11.3	50.0	25.6	81.1	34.6	-140.5	6.1	350.6	35.0	1.452	463.0	6.39	4.93	4.54
			BI	-60.8	12.4	177.2	12.7	55.7	42.8	154.3	53.3	-98.2	8.9	191.5	26.0	1.445	485.4	0.00	0.00	0.00
		dC	AI	-63.6	9.9	176.0	11.2	52.1	35.8	81.7	47.0	-147.6	9.0	348.2	44.7	1.463	427.4	5.46	4.79	5.09
			BI	-55.5	12.5	176.8	13.1	56.8	44.5	152.7	54.8	-107.9	13.2	188.0	30.1	1.454	456.6	0.00	0.00	0.00
		dG	AI	-71.9	6.5	174.6	7.6	48.4	17.8	82.0	30.1	-135.8	4.0	350.7	28.3	1.451	463.0	6.96	4.87	4.55
			BI	-62.2	12.4	175.6	14.2	54.9	45.1	154.6	52.0	-93.6	12.2	192.7	29.2	1.445	483.1	0.00	0.00	0.00
		dT	AI	-71.0	13.9	175.0	11.4	49.4	36.2	82.1	44.8	-136.3	9.0	351.5	34.8	1.461	438.6	6.51	5.52	5.21
			BI	-57.1	17.4	177.0	14.2	56.3	43.4	152.8	52.8	-107.8	13.5	186.9	35.1	1.454	463.0	0.00	0.00	0.00
Can		dA	AI	-58.0	13.4	152.2	15.1	52.8	33.7	86.5	33.9	-135.1	5.5	9.9	12.7	1.463	393.7	1.53	0.33	1.02
			BI	-43.8	8.8	151.0	9.7	55.7	37.3	144.3	36.2	-103.8	10.3	166.1	9.6	1.447	438.6	0.00	0.00	0.00
		dC	AI	-51.9	13.4	151.4	13.7	56.3	34.9	83.2	43.6	-155.6	12.2	11.4	18.1	1.481	362.3	0.00	0.00	0.01
			BI	-43.6	16.0	151.6	15.8	59.8	36.1	140.6	30.1	-118.9	8.7	160.5	11.7	1.458	413.2	0.81	1.09	0.00
		dG	AI	-58.0	12.3	151.5	15.2	51.7	32.4	87.6	26.3	-131.0	3.9	9.9	9.3	1.462	392.2	0.00	0.38	0.00
			BI	-42.9	8.4	150.1	8.6	54.4	34.0	144.7	37.5	-100.3	10.8	166.6	8.8	1.447	432.9	0.60	0.00	0.79
		dT	AI	-59.6	20.7	155.6	16.3	54.2	33.4	84.0	39.3	-145.2	7.3	18.5	14.2	1.479	350.9	0.44	0.00	0.55
			BI	-47.5	15.6	156.2	13.0	58.0	39.0	141.0	31.6	-115.3	11.3	159.2	13.1	1.457	418.4	0.00	0.32	0.00

Note: [a] For definition of conformational parameters see Fig. 1 and ref. 1 in the main text. [b] ΔE_{VAC} and ΔG_{VAC} are electronic and Gibbs energies *in vacuo*, calculated at the B3LYP-D3/6-311++G(d,p) level of theory, ΔE_{CPCM} is electronic energy calculated at the B3LYP-D3/6-311++G(d,p) level of theory using the CPCM model for water for geometries optimized *in vacuo* at the same theoretical level.

Table S2. Vibrational root-mean-square (VRMS) deviations (in degrees) at T = 0K and T = 298 K for the main conformational parameters (α, β, γ, δ, χ, and *P*, Figure 1 and Figure S1) in 2′-deoxyribonucleotide-5′-monophosphates (dNs) with variously modified sugar residues. Each modification has an individual number and belongs to one of the four groups (Figure 1): UNS (unsaturated), LOC (locked), HET (hetetocyclic), and FLR (fluorinated). The canonical (CAN) nucleotides were also analyzed and served as reference structures to understand the effect of individual chemical modifications.

				Conformational parameters													
				α		β		γ		δ		χ		P		l_{glycos}	
				0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K
UNS	**1**	dA	DNA	6.1	11.5	5.2	11.4	5.7	8.3	-	-	6.3	14.4	-	-	0.049	0.052
		dC	DNA	6.1	10.8	5.3	10.4	5.7	8.0	-	-	6.6	19.2	-	-	0.050	0.052
		dG	DNA	6.2	12.2	5.4	12.4	5.7	8.5	-	-	6.2	14.3	-	-	0.048	0.050
		dT	DNA	5.9	9.9	5.2	12.1	5.8	8.5	-	-	6.2	14.7	-	-	0.050	0.052
	2	dA	DNA	6.3	11.9	5.3	11.6	5.6	8.1	-	-	6.2	15.5	-	-	0.048	0.050
		dC	DNA	6.2	11.2	5.3	10.5	5.6	8.0	-	-	6.2	16.3	-	-	0.049	0.052
		dG	DNA	6.2	12.2	5.5	13.1	5.6	8.3	-	-	6.2	15.3	-	-	0.048	0.050
		dT	DNA	5.8	9.8	5.3	13.2	5.8	8.5	-	-	6.0	13.5	-	-	0.049	0.051
	3	dA	DNA	6.1	11.7	5.3	12.2	5.5	8.0	-	-	6.2	15.0	-	-	0.049	0.052
		dC	DNA	6.2	11.2	5.2	10.5	5.5	7.9	-	-	6.3	17.4	-	-	0.050	0.051
		dG	DNA	6.3	12.5	5.5	13.5	5.6	8.8	-	-	6.3	15.7	-	-	0.049	0.052
		dT	DNA	5.9	10.1	5.4	14.5	5.7	8.7	-	-	6.1	14.6	-	-	0.049	0.052
	4	dA	DNA	6.5	12.7	5.4	12.9	5.6	8.3	-	-	6.1	13.9	-	-	0.048	0.050
		dC	DNA	6.6	12.8	5.3	12.4	5.6	8.1	-	-	5.8	13.2	-	-	0.048	0.050
		dG	DNA	6.5	12.4	5.4	13.2	5.6	8.2	-	-	6.1	12.7	-	-	0.048	0.051
		dT	DNA	6.1	10.8	5.1	11.8	5.7	8.1	-	-	5.9	14.1	-	-	0.048	0.050
	5	dA	DNA	6.7	13.5	6.2	21.2	5.7	8.5	-	-	6.6	21.1	-	-	0.048	0.050
		dC	DNA	6.4	11.6	5.6	14.1	5.7	8.4	-	-	5.7	10.2	-	-	0.049	0.051
		dG	DNA	6.5	13.1	6.2	20.2	5.6	8.9	-	-	6.3	15.9	-	-	0.048	0.053
		dT	DNA	6.4	12.0	5.8	17.1	5.7	8.6	-	-	6.4	15.8	-	-	0.050	0.053
	6	dA	AI	6.1	13.1	5.5	16.2	5.5	8.5	5.1	8.3	5.8	16.4	6.9	9.8	0.049	0.051
			BI	6.4	12.1	5.4	11.8	5.4	8.0	4.6	7.0	6.4	15.8	7.3	11.1	0.047	0.049
		dC	AI	6.3	12.8	5.6	15.2	5.6	8.4	5.1	7.6	5.5	14.3	6.7	9.0	0.049	0.051
			BI	6.3	12.3	5.3	12.2	5.4	8.2	4.6	7.0	6.4	17.3	7.2	10.1	0.048	0.050
		dG	AI	6.2	13.5	5.5	15.8	5.5	8.5	5.1	8.1	5.8	16.9	6.9	9.5	0.049	0.054
			BI	6.4	12.2	5.3	11.5	5.4	8.3	4.7	7.2	6.3	15.5	7.2	10.6	0.048	0.050
		dT	AI	6.0	11.1	5.4	13.7	5.4	8.0	5.1	7.1	5.7	14.9	7.1	9.3	0.049	0.051
			BI	6.2	11.0	5.3	12.1	5.5	8.1	4.7	7.1	6.1	14.5	7.1	9.5	0.048	0.050

				Conformational parameters													
				α		β		γ		δ		χ		P		l_{glycos}	
				0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K
LOC	**7**	dA	AI	6.2	13.3	5.4	12.6	5.7	9.2	5.1	6.2	5.9	15.4	5.1	6.3	0.048	0.050
		dC	AI	6.3	14.1	5.5	13.4	5.5	8.3	5.1	6.2	5.1	9.4	4.9	6.1	0.049	0.052
		dG	AI	6.1	14.0	5.4	12.8	5.6	8.9	5.0	6.6	5.8	14.8	5.1	6.5	0.048	0.052
		dT	AI	6.2	11.6	5.4	11.8	5.6	8.4	5.1	6.1	5.4	11.6	5.0	6.1	0.050	0.052
HET	**8**	dA	AI	6.2	12.7	5.4	13.0	5.8	8.4	-	-	6.3	18.4	8.6	12.3	0.049	0.050
			BI	6.6	13.3	5.8	12.9	5.5	8.0	-	-	6.4	14.3	9.3	15.3	0.047	0.049
		dC	AI	6.2	12.4	5.4	13.1	5.7	8.4	-	-	5.5	13.3	7.9	10.5	0.050	0.053
			BI	6.2	11.2	5.3	11.5	5.5	8.0	-	-	6.4	15.1	9.8	14.9	0.048	0.050
		dG	AI	6.2	13.3	5.4	12.8	5.7	8.6	-	-	6.5	20.3	8.6	12.0	0.049	0.050
			BI	6.7	13.9	5.9	14.2	5.5	8.2	-	-	6.3	14.2	9.3	15.7	0.047	0.049
		dT	AI	5.9	10.3	5.3	12.4	5.8	8.9	-	-	6.0	16.2	8.3	11.4	0.051	0.055
			BI	6.1	11.0	5.5	12.9	5.4	7.7	-	-	6.2	13.5	9.5	14.4	0.048	0.050
	9	dA	AI	6.0	11.9	5.2	11.5	5.4	8.5	-	-	6.3	21.0	9.0	14.3	0.049	0.050
			BI	6.4	13.2	5.8	14.4	5.0	7.2	-	-	6.4	14.1	9.1	15.3	0.047	0.050
		dC	AI	6.0	11.7	5.3	11.7	5.4	8.3	-	-	5.3	11.0	8.2	11.0	0.050	0.052
			BI	6.10	10.8	5.4	12.3	5.0	7.5	-	-	6.5	15.8	9.0	14.0	0.049	0.050
		dG	AI	6.0	12.4	5.3	12.3	5.5	8.6	-	-	7.3	40.0	9.5	24.3	0.048	0.050
			BI	6.6	14.0	6.1	16.5	5.1	7.5	-	-	6.3	14.3	9.2	16.0	0.048	0.051
		dT	AI	5.8	10.2	5.2	12.3	5.6	8.7	-	-	5.8	14.8	8.2	11.0	0.050	0.052
			BI	6.1	11.3	5.7	15.4	5.1	7.4	-	-	6.3	14.1	8.8	13.4	0.048	0.051
FLR	**10**	dA	AI	6.1	13.0	5.2	11.7	5.6	8.3	5.0	7.3	6.2	18.2	8.4	11.9	0.048	0.050
			BI	6.7	14.1	5.9	14.2	5.3	7.8	4.6	7.1	6.3	13.9	8.8	14.6	0.047	0.049
		dC	AI	6.2	12.6	5.3	12.2	5.6	8.3	5.0	6.8	5.3	11.8	7.6	10.1	0.050	0.053
			BI	6.3	11.2	5.4	11.4	5.4	7.8	4.6	7.3	6.1	13.3	8.4	12.4	0.048	0.050
		dG	AI	6.2	13.4	5.3	12.4	5.6	8.8	5.1	7.5	6.3	18.8	8.6	12.9	0.048	0.052
			BI	6.6	17.1	6.0	17.3	5.7	9.7	4.7	7.7	7.0	20.4	8.8	16.8	0.047	0.049
		dT	AI	5.9	10.5	5.2	12.1	5.7	8.6	5.0	7.1	5.9	15.9	7.8	10.5	0.049	0.053
			BI	6.3	11.6	5.6	13.4	5.3	7.7	4.7	7.2	6.0	12.2	8.2	11.9	0.048	0.049
	11	dA	AI	6.2	12.5	5.3	11.7	5.6	8.2	5.1	8.9	6.3	19.9	10.0	15.3	0.048	0.050
			BI	8.3	27.2	7.2	24.8	5.5	9.5	5.4	12.4	6.5	16.3	14.1	34.5	0.047	0.049
		dC	AI	6.3	12.4	5.3	11.8	5.5	7.8	5.1	7.7	5.7	13.8	9.7	14.8	0.049	0.051
			BI	6.6	13.4	5.7	13.1	5.4	9.0	6.2	18.9	6.2	14.7	15.1	39.1	0.048	0.050
		dG	AI	6.2	13.4	5.3	12.5	5.6	8.6	5.1	8.2	6.2	19.8	9.4	15.1	0.048	0.052
			BI	7.6	21.4	7.0	22.1	5.4	8.6	5.3	11.4	6.3	15.0	14.1	30.2	0.047	0.048
		dT	AI	6.0	10.5	5.2	11.6	5.6	8.2	5.1	7.5	5.7	13.4	8.3	14.1	0.049	0.050
			BI	6.4	12.5	5.5	13.2	5.3	8.0	5.7	14.5	6.1	13.0	14.0	31.1	0.048	0.050

				Conformational parameters													
				α		β		γ		δ		χ		P		l_{glycos}	
				0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K	0K	298K
FLR	**12**	dA	AI	6.1	12.6	5.3	11.6	5.5	8.0	5.0	7.7	6.1	16.6	9.4	14.9	0.048	0.051
			BI	7.4	19.4	6.5	18.1	5.4	8.6	5.1	9.7	6.2	14.0	12.8	25.5	0.047	0.049
		dC	AI	6.2	12.1	5.3	11.6	5.4	7.6	5.0	7.4	5.7	14.2	9.1	13.2	0.049	0.051
			BI	6.4	12.2	5.5	12.2	5.3	8.1	5.1	10.2	5.9	12.6	12.5	22.0	0.048	0.050
		dG	AI	6.1	13.4	5.3	11.9	5.5	7.9	5.1	7.6	6.0	17.0	9.0	13.7	0.047	0.049
			BI	7.0	16.5	6.2	16.0	5.4	8.2	4.9	9.0	6.2	13.8	12.9	24.6	0.047	0.049
		dT	AI	5.9	10.3	5.2	11.7	5.5	8.2	5.0	7.4	5.7	13.6	8.9	13.4	0.049	0.052
			BI	6.3	13.2	6.5	11.6	5.9	11.2	5.4	10.7	6.5	9.8	6.2	13.6	0.047	0.050
	13	dA	AI	8.2	6.3	5.2	14.4	5.7	9.9	5.2	10.0	6.2	23.1	6.2	9.6	0.047	0.050
			BI	6.4	12.8	5.4	12.5	5.4	7.7	4.5	6.8	6.1	14.8	6.8	10.7	0.047	0.049
		dC	AI	6.5	13.3	5.4	13.2	5.7	8.8	5.1	7.8	5.7	16.2	6.0	8.0	0.049	0.052
			BI	6.4	13.6	5.3	12.1	5.3	7.5	4.6	6.9	5.9	13.9	6.5	9.1	0.048	0.051
		dG	AI	6.4	12.6	5.3	12.5	5.6	8.1	5.2	9.3	5.9	12.5	7.6	12.9	0.047	0.050
			BI	6.6	13.0	5.3	11.9	5.4	7.6	4.6	7.0	6.2	15.0	6.8	11.0	0.047	0.050
		dT	AI	6.2	12.0	5.2	12.2	5.6	7.8	5.1	7.7	5.8	15.8	6.7	9.6	0.048	0.050
			BI	6.0	10.5	5.1	11.6	5.4	7.5	4.6	6.9	5.9	12.9	6.4	8.8	0.047	0.049
	14	dA	AI	6.3	15.9	5.2	13.3	5.6	9.3	5.0	8.1	5.9	18.1	5.9	8.5	0.046	0.049
			BI	6.5	12.9	5.4	12.6	5.3	7.4	4.5	6.5	6.2	15.1	6.2	9.6	0.047	0.050
		dC	AI	6.5	14.3	5.4	13.4	5.6	8.0	5.0	7.1	5.6	15.0	5.9	7.8	0.048	0.050
			BI	6.4	12.8	5.3	12.4	5.3	7.3	4.4	6.5	5.7	12.5	6.1	9.1	0.048	0.049
		dG	AI	6.4	17.5	5.3	16.2	5.6	10.9	5.1	8.6	6.0	22.2	6.1	9.3	0.046	0.048
			BI	6.5	12.9	5.3	11.9	5.3	7.3	4.5	6.6	6.0	13.1	6.2	9.2	0.046	0.050
		dT	AI	6.2	12.2	5.2	13.3	5.6	8.0	5.0	7.2	5.8	14.9	6.3	8.6	0.048	0.050
			BI	6.2	11.0	5.2	12.0	5.4	7.4	4.5	6.6	5.8	12.4	6.1	8.5	0.047	0.049
CAN		dA	AI	6.1	12.4	5.3	11.6	5.6	8.3	5.1	8.1	6.2	19.0	9.3	13.5	0.049	0.053
			BI	6.9	15.2	5.9	14.4	5.3	7.9	4.8	7.8	6.4	14.2	9.4	15.1	0.047	0.049
		dC	AI	6.1	12.4	5.3	12.2	5.5	8.2	5.1	7.4	5.5	12.9	8.4	11.5	0.047	0.049
			BI	6.3	11.4	5.4	11.3	5.4	8.0	5.0	8.4	6.4	15.3	9.2	13.9	0.050	0.052
		dG	AI	6.1	12.9	5.2	11.6	5.6	8.4	5.2	9.1	6.4	22.4	9.8	15.5	0.049	0.050
			BI	7.0	15.5	6.1	15.2	5.4	8.2	4.8	7.6	6.3	13.8	9.3	15.7	0.047	0.050
		dT	AI	5.8	10.1	5.1	11.2	5.6	8.3	5.2	7.7	6.0	16.6	9.0	12.8	0.050	0.052
			BI	6.2	11.5	5.4	12.4	5.4	7.8	4.9	8.2	6.2	13.5	8.9	13.2	0.048	0.050

Table S3. Electron density topological characteristics of hydrogen (H) bonds in dNs with the sugar residue **9** (**Fig. 1** in the main text) as identified by QTAIM analysis. The wavefunctions for QTAIM analysis were calculated using the the Gaussian 09 package at the B3LYP-D3/6-311++G(d,p) level of theory corresponding to optimized geometries. The pseudo-hydrogen bonds CH···S are highlighted in red.

Nucleotide	Conformer	H-bond	ρ^a	$\Delta\rho^b$	$E_{HB}{}^c$
dA	AI	C8H···O5'	0.013	0.045	2.5
		C8H···S3'	0.007	0.023	1.1
	BI	C2'H···O5'	0.011	0.039	2.2
		C8H···OA	0.013	0.041	2.4
dC	AI	C6H···O5'	0.020	0.073	4.3
		C5H···OA	0.002	0.010	0.4
	BI	C2'H···O5'	0.007	0.028	1.5
		C6H···O5'	0.012	0.039	2.3
		C1'H···O2	0.020	0.084	4.6
		C6H···OA	0.010	0.032	1.9
dG	AI	C8H···O5'	0.012	0.040	2.3
		C8H···S3'	0.007	0.024	1.1
	BI	C2'H···O5'	0.011	0.040	2.3
		C8H···OA	0.013	0.040	2.3
dT	AI	C6H···O5'	0.016	0.055	3.1
		C6H···S3'	0.007	0.026	1.3
		C5H (met)···OA	0.012	0.039	2.3
	BI	C2'H···O5'	0.008	0.030	1.7

Note: [a] Electron density at the bond critical point, atomic units (a.u.); [b] Laplacian of the electron density at bond critical point, a.u.; [c] H-bond energy calculated by means of Espinosa-Molins-Lecomte formula (*Chem. Phys. Lett.*, 1998, **285**, 170).