SUPPORTING INFORMATION

Exploring non-covalent interactions in guanine- and xanthine-based model DNA quadruplex structures: A comprehensive quantum chemical approach

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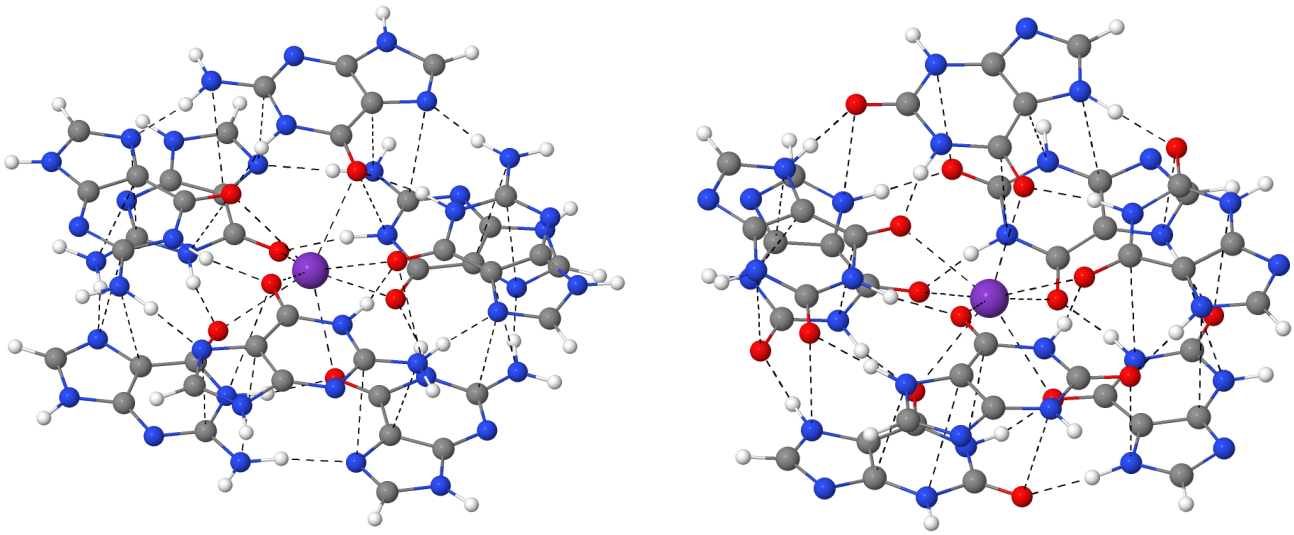

Figure S1. Optimized structures of guanine (left) and xanthine (right) $(B4)_2$ complexes with a K^+ ion inside the central channel. Dotted lines designate non-covalent interactions (H-bonds, ion-base coordination, and van der Waals contacts) identified by the QTAIM approach. Wavefunctions for QTAIM analysis were calculated at the BLYP/def2-TZVPP level of theory in Gaussian 09 for TURBOMOLE geometries.

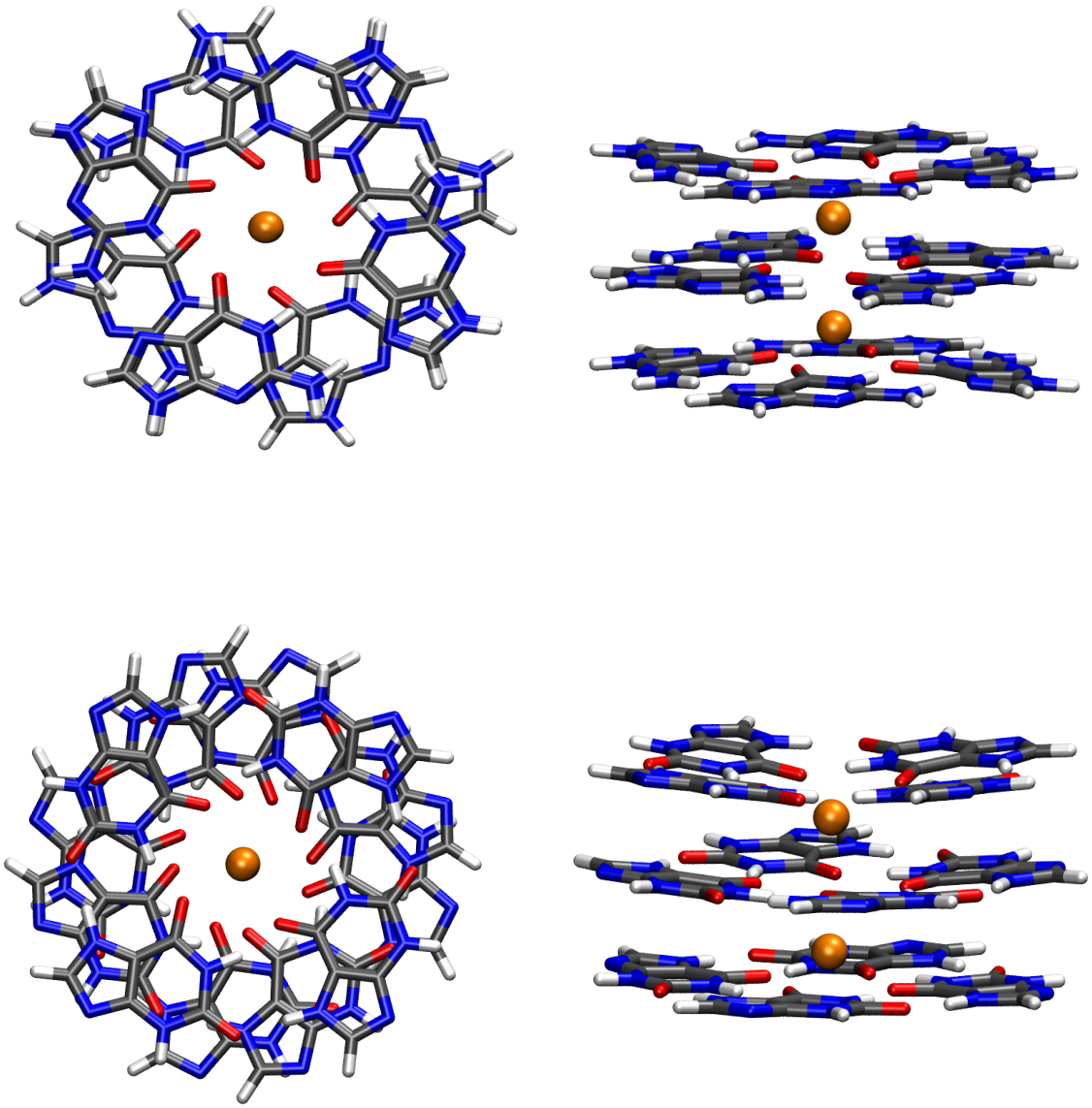

Figure S2. Optimized structures of Gua (upper) and Xan (lower) $(B4)_3$ complexes with two Na^+ ions. The structures on the left display the view from the top, whereas complexes on the right show the lateral view.

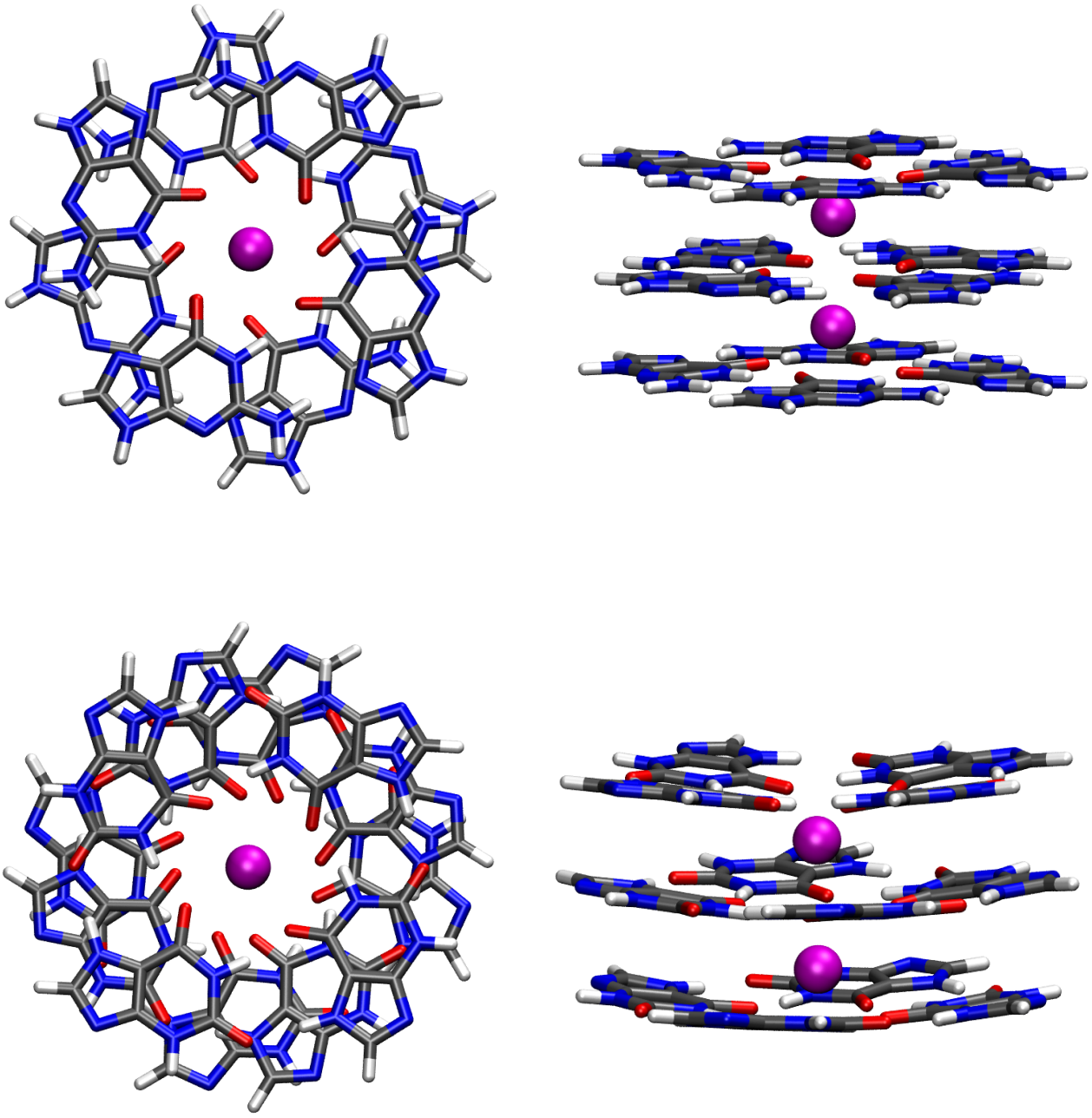

Figure S3. Optimized structures of Gua (upper) and Xan (lower) $(B4)_3$ complexes with two K^+ ions. The structures on the left display the view from the top, whereas complexes on the right show the lateral view.

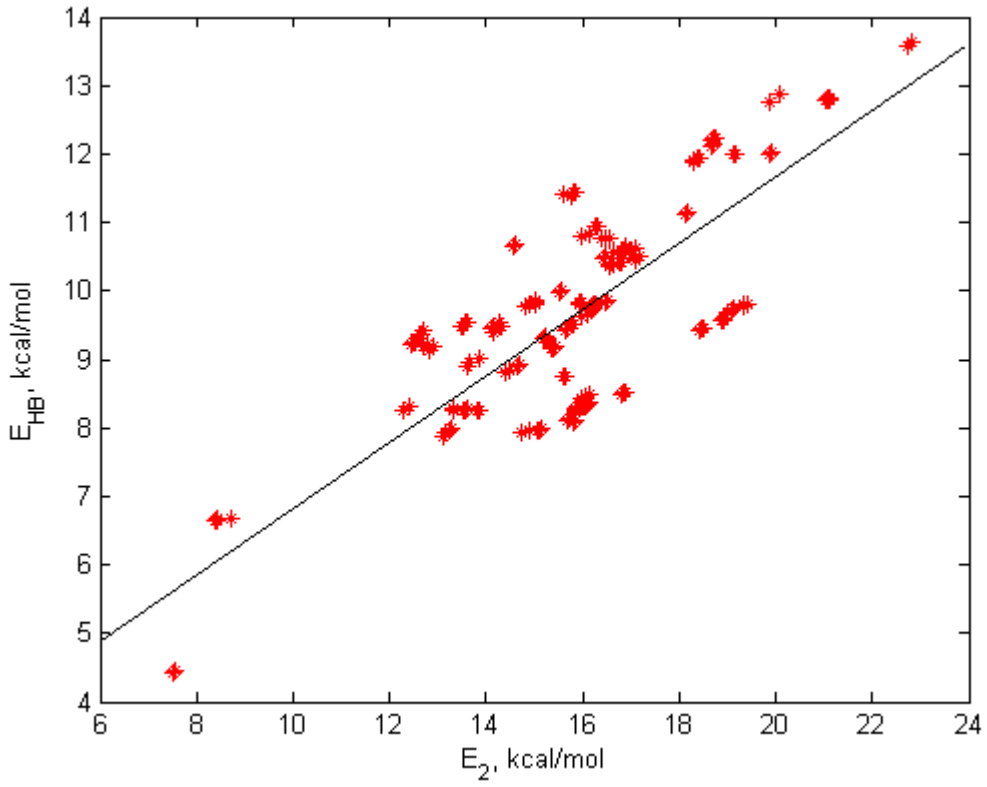

Figure S4. Correlation between the H-bond energy calculated by the EML formula and the donor-acceptor LP-BD* stabilization energy from NBO analysis (LP – lone pair(s) of the H-bond acceptor atom, BD* is the anti-bonding orbital of the H-bond donor group).

Table S1. Van der Waals volumes of Gua and Xan B4 and $(B4)_2$ DNA quadruplex models with/without Na^+/K^+. The geometries were optimized at the BLYP-D3/def2-TZVPP level of theory. Volumes were calculated by using the Vega ZZ program. Volume units are $Å^3$.

Structure	Xan	Gua
B	115	117
B4	444	467
$B4 \cdot Na^+$	476	496
$B4 \cdot K^+$	514	530
$(B4)_2$	886	930
$(B4)_2 \cdot Na^+$	919	934
$(B4)_2 \cdot K^+$	928	956

Table S2. Formation energies ΔE_{form} (in kcal/mol) of model quadruplex structures obtained at the BLYP-D3/def2–TZVPP level of theory using the COSMO model of water in TURBOMOLE. ΔE_{form} was calculated as the difference between the electronic energy of the whole optimized complex and its components (formula (1) in the manuscript).

Components/Optimized structure	ΔE_{form} (B = Gua)	ΔE_{form} (B = Xan)
$4*B \rightarrow B4$	-33	-30
$4*B + Na^+ \rightarrow B4 \cdot Na^+$	-63	-55
$4*B + K^+ \rightarrow B4 \cdot K^+$	-57	50
$8*B \rightarrow (B4)_2$	-89	-87
$(B4)_2 + Na^+ \rightarrow (B4)_2 \cdot Na^+$	-58	-44
$(B4)_2 + K^+ \rightarrow (B4)_2 \cdot K^+$	-55	-42
$12*B \rightarrow (B4)_3$	-139	-145
$(B4)_3 + Na^+ \rightarrow (B4)_3 \cdot Na^+$	-66	-49
$(B4)_3 + K^+ \rightarrow (B4)_3 \cdot K^+$	-63	-45
$(B4)_3 \cdot Na^+ + Na^+ \rightarrow (B4)_3 \cdot 2Na^+$	-52	-35
$(B4)_3 \cdot K^+ + K^+ \rightarrow (B4)_3 \cdot 2K^+$	-48	-29

Table S3. Energetic contributions of H-bonding, stacking, and ion coordination to the total interaction energy ΔE_{int} in model guanine and xanthine quadruplex structures. The optimization of the geometry and subsequent EDA were performed at the BLYP-D3/TZP level of theory. The molecular regions were chosen in a way that allows separating the contributions from all three major types of non-covalent interactions (H-bonding, stacking, and ion coordination). All units are kcal/mol.

Base	Model	H-bonding[a]	Stacking[b]	Coordination[c]	ΔE_{int}[d]
Gua	B4	-88	-	-	-88
	$B4 \cdot Na^+$	-90	-	-111	-201
	$B4 \cdot K^+$	-90	-	-84	-174
	$(B4)_2$	-179	-34	-	-213
	$(B4)_2 \cdot Na^+$	-177	-34	-149	-360
	$(B4)_2 \cdot K^+$	-179	-34	-126	-339
	$(B4)_3$	-267	-70	-	-337
	$(B4)_3 \cdot 2Na^+$	-264	-66	-207	-537
	$(B4)_3 \cdot 2K^+$	-269	-67	-159	-495
Xan	B4	-76	-	-	-76
	$B4 \cdot Na^+$	-75	-	-90	-165
	$B4 \cdot K^+$	-76	-	-66	-142
	$(B4)_2$	-152	-42	-	-194
	$(B4)_2 \cdot Na^+$	-151	-38	-121	-310
	$(B4)_2 \cdot K^+$	-150	-40	-98	-288
	$(B4)_3$	-228	-85	-	-313
	$(B4)_3 \cdot 2Na^+$	-220	-88	-146	-454
	$(B4)_3 \cdot 2K^+$	-222	-85	-96	-403

Note: Energetic contributions of H-bonding, stacking, and ion coordination to the total interaction energies were evaluated in the following way. The H-bond energy was calculated as the sum of the interaction energies between four bases (regions 1, 2, 3 and 4) in each individual tetrad in the structure. Stacking was calculated as the interaction energy between two (in the case of two-stack models) or three (in three-stack structures) tetrads representing individual regions. The ion coordination energy was estimated as the interaction energy between the Na^+/K^+ ion (region 1) and the rest of the system (region 2). In the case of $(B4)_3 \cdot 2M^+$ models the ion coordination energy was the sum of the individual ion coordination interactions for both ions. ΔE_{int} was calculated as the interaction energy between all the monomeric units (bases and ions) in a structure, each representing a separate region. The ΔE_{int} energy is equal to the sum of the H-bonding, stacking, and ion coordination contributions.

Table S4. QTAIM and geometric characteristics of individual H-bonds and van der Waals contacts in B4 and $(B4)_2$ models for Gua and Xan. The geometries were optimized in TURBOMOLE at the BLYP-D3/def2-TZVPP level of theory. The wavefunctions for QTAIM analysis were obtained at the BLYP/def2-TZVPP level of theory in Gaussian 09.

Structure	Interaction	N[a]	ρ[b]	$\Delta\rho$[b]	E_{bond} [c]	ΣE_{HB} [d]	$d_{A...B}$ [e]	$d_{H...B}$ [f]	AHB [g]
G4 (fully optimized)	N1H···O6	4	0.037	0.096÷0.097	10.76 [6.30]	78.01	2.82÷2.83	1.79÷1.80	170.8÷171.0
	N2H···N7	4	0.035	0.074	8.74		2.92	1.90	169.9÷170.0
G4 (planar)	N1H···O6	4	0.036	0.095	9.80÷9.82 [6.07]	71.69	2.83	1.80	169.6
	N2H···N7	4	0.035	0.074	8.09÷8.12		2.92	1.90	170.5÷170.6
$G4{\cdot}Na^+$ (fully optimized)	O6···Na^+	4	0.020	0.133÷0.134	-	67.18	2.31	-	-
	N1H···O6	4	0.032	0.088	8.24÷8.32 [5.17]		2.87÷2.88	1.86÷1.87	164.4÷164.5
	N2H···N7	4	0.036	0.075	8.50-8.53		2.91	1.88	173.6÷173.7
$G4{\cdot}K^+$ (fully optimized)	O6···K^+	4	0.014÷0.015	0.068÷0.076	-	68.00	2.74÷2.79	-	-
	N1H···O6	4	0.033÷0.034	0.090÷0.091	8.90÷9.02 [5.40-5.62]		2.86	1.84	166.8÷167.5
	N2H···N7	4	0.034÷0.035	0.073÷0.074	7.92÷8.13		2.93	1.90	171.7÷173.4
$(G4)_2$ (fully optimized)	C2···C5	4	0.007	0.020	-	151.49	3.26÷3.27	-	-
	N3···N7	4	0.007	0.026	-		3.25÷3.27	-	-
	N2···N7	4	0.007	0.024	-		3.25÷3.27	-	-
	N2···C4	1	0.006	0.020	-		3.37	-	-
	O6···N1	4	0.002	0.007	-		3.80÷3.88	-	-
	N1H···O6	8	0.038	0.098÷0.099	10.49÷10.66 [6.52]		2.81÷2.82	1.78	169.9÷172.6
	N2H···N7	8	0.035÷0.036	0.075÷0.076	8.26÷8.49		2.90÷2.91	1.88÷1.89	167.8÷168.3
$(G4)_2$ (planar)	O6···N1	4	0.003	0.011	-	151.96	3.56÷3.57	-	-
	N2···C4	4	0.006	0.021	-		3.27÷3.28	-	-
	N2···N7	3	0.006	0.024	-		3.27	-	-
	N3 ···N2	1	0.006	0.024	-		3.27	-	-
	N3···N7	4	0.006	0.023	-		3.32	-	-
	C2···C5	4	0.006	0.020	-		3.26	-	-
	N1H···O6	8	0.038÷0.039	0.099÷0.101	10.58÷11.15 [6.52÷6.75]		2.80÷2.81	1.76÷1.78	171÷171.2
	N2H···N7	8	0.034÷0.035	0.074÷0.075	7.96÷8.31		2.91÷2.92	1.89÷1.90	167.2÷167.9
$(G4)_2{\cdot}Na^+$ (fully optimized)	O6···N1	8	0.005	0.022	-	153.82	3.27÷3.29	-	-
	O6···O6	8	0.004÷0.005	0.017÷0.018	-		3.32÷3.36	-	-
	O6···Na^+	8	0.006÷0.010	0.031÷0.058	-		2.59÷2.80	-	-
	N2···C5	8	0.006	0.020	-		3.40÷3.41	-	-
	C2···N7	8	0.006	0.022÷0.023	-		3.20÷3.21	-	-
	N1H···O6	8	0.035÷0.036	0.092÷0.094	9.45÷9.87 [5.85÷6.07]		2.83÷2.84	1.81÷1.82	164.1÷165.7
	N2H···N7	8	0.039÷0.040	0.077÷0.078	9.41÷9.75		2.87÷2.88	1.84÷1.85	172.5÷173.4
$(G4)_2{\cdot}Na^+$ (planar)	C2···N7	4	0.006	0.022÷0.023	-	154.51	3.23÷3.24	-	-
	N2···C5	8	0.006	0.021	-		3.39÷3.40	-	-
	O6···N1	8	0.005÷0.006	0.018÷0.019	-		3.35÷3.36	-	-
	N3···N7	4	0.006	0.023	-		3.34	-	-
	O6···Na^+	8	0.006÷0.009	0.029÷0.051	-		2.63÷2.83	-	-
	N1H···O6	8	0.035÷0.036	0.092÷0.094	9.47÷9.83 [5.85÷6.07]		2.83÷2.84	1.81÷1.82	163.9÷165.3
	N2H···N7	8	0.040	0.077÷0.078	9.58÷9.78		2.87÷2.88	1.84	173.4÷174.2
$(G4)_2{\cdot}K^+$ (fully optimized)	O6···K^+	8	0.012÷0.013	0.060÷0.064	-	141.12	2.81÷2.84	-	-
	O6···N1	4	0.004	0.017	-		3.39÷3.40	-	-
	N2···C5	8	0.006	0.019	-		3.40÷3.42	-	-
	C2···N7	8	0.006	0.021	-		3.25	-	-
	N1H···O6	8	0.034÷0.035	0.092÷0.093	9.22÷9.42 [5.62÷5.65]		2.84÷2.85	1.82÷1.83	167.4÷167.8
	N2H···N7	8	0.036	0.074	8.30÷8.37		2.92	1.89	171.1÷171.5

X4 (fully optimized)	N1H···O6	4	0.036	0.096	9.99÷10.02 [6.07]	81.62 [49.92]	2.82	1.80	167.2÷167.4
	N7H···O2	4	0.037÷0.038	0.095÷0.096	10.38÷10.43 [6.30÷6.52]		2.82	1.78	173.8÷174.0
X4 (planar)	N1H···O6	4	0.042	0.103	12.01÷12.02 [7.42]	81.10 [50.36]	2.77	1.74	167.6÷167.7
	N7H···O2	4	0.032	0.086	8.24 [5.17]		1.89	1.86	179.3
$X4{\cdot}Na^+$ (fully optimized)	O6···Na^+	4	0.018	0.117÷0.119	-	77.16 [47.68]	2.35÷2.36	-	-
	N1H···O6	4	0.035	0.094	9.48÷9.53 [5.85]		2.83	1.82	163.8÷164.2
	N7H···O2	4	0.036	0.092	9.77÷9.80 [6.07]		2.84	1.80	173.7÷174.2
$X4{\cdot}K^+$ (fully optimized)	O6···K^+	4	0.013÷0.014	0.066÷0.068	-	78.46 [48.34]	2.79÷2.80	-	-
	N1H···O6	4	0.034	0.093	9.12÷9.23 [5.62]		2.84÷2.85	1.83	166.2÷166.4
	N7H···O2	4	0.037÷0.038	0.095	10.37÷10.50 [6.30÷6.52]		2.81÷2.82	1.78÷1.79	172.4÷173.1
$(X4)_2$ (fully optimized)	O2···N3	4	0.004÷0.005	0.018	-	174.23 [107.73]	3.36	-	-
	N3···C5	4	0.007	0.022	-		3.30÷3.31	-	-
	N1···C6	4	0.006	0.021	-		3.26	-	-
	N3···N7	4	0.007	0.027	-		3.24	-	-
	N7···O2	4	0.007	0.028	-		3.15	-	-
	N1H···O6	8	0.042÷0.044	0.103÷0.106	11.99÷12.80 [7.42÷7.87]		2.75÷2.77	1.72÷1.74	168.2÷170.6
	N7H···O2	8	0.034÷0.035	0.091÷0.092	9.33÷9.44 [5.62÷5.85]		2.85	1.81÷1.82	174.5÷178.0
$(X4)_2$ (planar)	C2···C5	4	0.007	0.021	-	174.04 [107.04]	3.24÷3.25	-	-
	O6···N1	4	0.002÷0.003	0.009÷0.010	-		3.63÷3.66	-	-
	N3···N7	4	0.006	0.025	-		3.30	-	-
	N7···O2	4	0.006	0.024	-		3.19	-	-
	O2···N3	3	0.006	0.023	-		3.24	-	-
	O6···N3	1	0.006	0.023	-		3.24	-	-
	N1H···O6	8	0.044÷0.046	0.106÷0.109	12.79÷13.63 [7.87÷8.32]		2.73÷2.75	1.70÷1.72	169÷169.3
	N7H···O2	8	0.032÷0.033	0.086÷0.089	8.24÷8.85 [5.17÷5.40]		2.87÷2.89	1.83÷1.86	177.6÷178.0
$(X4)_2{\cdot}Na^+$ (fully optimized)	O6···N1	7	0.002÷0.003	0.009÷0.010	-	174.77 [107.04]	3.63÷3.66	-	-
	O2···N3	3	0.006	0.023	-		3.24	-	-
	C2···C5	3	0.007	0.021	-		3.24÷3.25	-	-
	N3···N7	4	0.006	0.025	-		3.30	-	-
	N1···C6	4	0.007	0.026	-		3.14	-	-
	O6···O6	3	0.005÷0.006	0.022	-		3.21÷3.23	-	-
	O6···Na^+	8	0.007÷0.008	0.037÷0.045	-		2.67÷2.75	-	-
	N1H···O6	8	0.042÷0.044	0.102÷0.105	11.89÷12.86 [7.42÷7.87]		2.74÷2.77	1.72÷1.75	165.4÷165.6
	N7H···O2	8	0.034÷0.036	0.089÷0.092	9.15÷9.74 [5.62÷6.07]		2.84÷2.86	1.81÷1.83	178.5÷178.9
$(X4)_2{\cdot}Na^+$ (planar)	C2···C5	4	0.007	0.022	-	174.32 [107.70]	3.24	-	-
	N1···C6	4	0.007	0.024	-		3.18÷3.19	-	-
	O6···N1	4	0.003	0.013	-		3.48	-	-
	N3···N7	4	0.006÷0.007	0.026	-		3.27÷3.28	-	-
	N7···O2	4	0.006	0.024÷0.025	-		3.19	-	-
	O6···O6	4	0.005÷0.006	0.022	-		3.21÷3.23	-	-
	O6···Na^+	8	0.002	0.042÷0.045	-		2.67÷2.70	-	-
	N1H···O6	8	0.042÷0.044	0.102÷0.105	11.79÷12.86 [7.42÷7.87]		2.74÷2.77	1.72÷1.75	165.4÷165.6
	N7H···O2	8	0.034÷0.036	0.089÷0.092	9.15÷9.74 [5.62÷6.07]		2.84÷2.86	1.81÷1.83	178.5÷178.9
$(X4)_2{\cdot}K^+$ (fully optimized)	O2···N3	4	0.004	0.018	-	157.07 [96.68]	3.35÷3.36	-	-
	N3···C5	4	0.006	0.021	-		3.35	-	-
	N1···C6	2	0.006	0.021	-		3.27	-	-
	N1···C5	2	0.006	0.021	-		3.27	-	-
	C4···N7	4	0.006	0.024	-		3.21	-	-
	N7···O2	4	0.006	0.026	-		3.17	-	-
	O6···K^+	8	0.012÷0.013	0.058÷0.062	-		2.82÷2.85	-	-
	N1H···O6	8	0.038÷0.040	0.099÷0.101	10.64÷11.45		2.78÷2.80	1.76÷1.78	166.4÷167.5

					[6.52÷6.97]				
	N7H···O2	8	0.032÷0.034	0.087÷0.089	8.26÷8.93 [5.17÷5.62]		2.87÷2.89	1.83÷1.86	174.3÷178.8

Note: [a] Number of times a particular interaction occurs in a structure; [b] Ranges (from minimal to maximal value) for the electron density and the Laplacian of the electron density at the bond critical point (BCP or (3,-1) critical point), atomic units; [c] Energy range (in kcal/mol) for H-bonds determined by EML formula (4). The values in brackets indicate alternative energy values for the NH···O hydrogen bonds calculated by formula $E_{NH...O} = -2.03 + 225 \cdot \rho$ (see Computational methodology section and Ref. 60). [d] Sum (in kcal/mol) of all the H-bond energies in a complex. For xanthine complexes containing only H-bonds of the NH···O type, the sum of the alternative energies (in brackets) was calculated; [e] Range (in Å) for the distance between atoms A and B in the case of hydrogen bonds AH···B. For van der Waals A···B contacts, this is the distance between two interacting atoms A and B. [f] Range (in Å) for the distance between hydrogen (H) and acceptor (B) atoms in the case of hydrogen bonds AH···B. [g] Range for the H-bond angle AHB (for H-bonds), degrees.

Table S5. NBO analysis of H-bonds in model Gua- and Xan-containing DNA quadruplex structures. The geometries were optimized at the BLYP-D3 level of theory in TURBOMOLE. NBO analysis was performed at the same level of theory in Gaussian 09. All characteristics are calculated as average values for each H-bond type.

Complex	H-bond	N[a]	E_2[b]	CT[c]	Q_A[d]	Q_H[d]	Q_B[d]
G4 (fully optimized)	N1H···O6	4	16.49	0.053	-0.559	0.448	-0.659
	N2H···N7	4	15.62	0.052	-0.750	0.430	-0.472
G4 (planar)	N1H···O6	4	15.94	0.052	-0.560	0.448	-0.657
	N2H···N7	4	15.87	0.052	-0.750	0.430	-0.472
G4·Na^+ (fully optimized)	N1H···O6	4	12.35	0.045	-0.549	0.447	-0.679
	N2H···N7	4	16.86	0.055	-0.745	0.430	-0.469
G4·K^+ (fully optimized)	N1H···O6	4	13.73	0.047	-0.549	0.446	-0.671
	N2H···N7	4	15.25	0.052	-0.741	0.428	-0.455
$(G4)_2$ (fully optimized)	N1H···O6 (T1)	4	16.60	0.054	-0.565	0.449	-0.660
	N2H···N7 (T1)	4	16.07	0.054	-0.760	0.430	-0.470
	N1H···O6 (T2)	4	16.97	0.054	-0.565	0.449	-0.659
	N2H···N7 (T2)	4	15.90	0.053	-0.753	0.432	-0.471
$(G4)_2$ (planar)	N1H···O6 (T1)	4	18.18	0.056	-0.566	0.450	-0.658
	N2H···N7 (T1)	4	15.86	0.053	-0.759	0.431	-0.469
	N1H···O6 (T2)	4	16.81	0.054	-0.564	0.450	-0.659
	N2H···N7 (T2)	4	15.09	0.051	-0.756	0.431	-0.472
$(G4)_2$·Na^+ (fully optimized)	N1H···O6 (T1)	4	14.91	0.052	-0.557	0.451	-0.658
	N2H···N7 (T1)	4	18.45	0.059	-0.757	0.430	-0.471
	N1H···O6 (T2)	4	14.18	0.051	-0.555	0.451	-0.667
	N2H···N7 (T2)	4	19.00	0.060	-0.755	0.430	-0.470
$(G4)_2$·Na^+ (planar)	N1H···O6 (T1)	4	15.02	0.052	-0.557	0.451	-0.659
	N2H···N7 (T1)	4	18.91	0.060	-0.756	0.431	-0.471
	N1H···O6 (T2)	4	14.22	0.051	-0.555	0.451	-0.670
	N2H···N7 (T2)	4	19.40	0.061	-0.755	0.430	-0.470
$(G4)_2$·K^+ (fully optimized)	N1H···O6 (T1)	4	12.46	0.047	-0.546	0.452	-0.602
	N2H···N7 (T1)	4	16.03	0.053	-0.752	0.432	-0.456
	N1H···O6 (T2)	4	12.62	0.047	-0.546	0.452	-0.605
	N2H···N7 (T2)	4	16.08	0.053	-0.752	0.432	-0.455
X4 (fully optimized)	N1H···O6	4	15.56	0.051	-0.574	0.451	-0.628
	N7H···O2	4	16.69	0.054	-0.455	0.458	-0.657
X4 (planar)	N1H···O6	4	19.91	0.058	-0.574	0.449	-0.626
	N7H···O2	4	13.82	0.047	-0.455	0.459	-0.656
X4·Na^+ (fully optimized)	N1H···O6	4	13.55	0.047	-0.563	0.448	-0.658
	N7H···O2	4	16.22	0.053	-0.453	0.458	-0.646
X4·K^+ (fully optimized)	N1H···O6	4	12.81	0.046	-0.573	0.444	-0.664
	N7H···O2	4	16.87	0.055	-0.460	0.456	-0.628
$(X4)_2$ (fully optimized)	N1H···O6 (T1)	4	19.15	0.058	-0.581	0.452	-0.625
	N7H···O2 (T1)	4	15.34	0.050	-0.458	0.459	-0.660
	N1H···O6 (T2)	4	21.09	0.060	-0.579	0.451	-0.626
	N7H···O2 (T2)	4	15.55	0.051	-0.464	0.462	-0.655
$(X4)_2$ (planar)	N1H···O6 (T1)	4	22.77	0.064	-0.583	0.452	-0.624
	N7H···O2 (T1)	4	14.43	0.049	-0.455	0.459	-0.660
	N1H···O6 (T2)	4	21.07	0.060	-0.578	0.451	-0.625

Complex	H-bond	N[a]	E_2[b]	CT[c]	Q_A[d]	Q_H[d]	Q_B[d]
$(X4)_2$ (planar)	N7H···O2 (T2)	4	13.58	0.047	-0.464	0.462	-0.656
$(X4)_2 \cdot Na^+$ (fully optimized)	N1H···O6 (T1)	4	18.71	0.057	-0.572	0.452	-0.647
	N7H···O2 (T1)	4	15.79	0.051	-0.455	0.458	-0.651
	N1H···O6 (T2)	4	18.69	0.057	-0.571	0.452	-0.632
	N7H···O2 (T2)	4	16.51	0.053	-0.463	0.460	-0.649
$(X4)_2 \cdot Na^+$ (planar)	N1H···O6 (T1)	4	19.96	0.059	-0.574	0.452	-0.642
	N7H···O2 (T1)	4	16.12	0.052	-0.455	0.458	-0.651
	N1H···O6 (T2)	4	18.35	0.056	-0.568	0.452	-0.638
	N7H···O2 (T2)	4	15.42	0.051	-0.464	0.461	-0.648
$(X4)_2 \cdot K^+$ (fully optimized)	N1H···O6 (T1)	4	14.57	0.049	-0.569	0.453	-0.591
	N7H···O2 (T1)	4	13.33	0.047	-0.461	0.457	-0.642
	N1H···O6 (T2)	4	15.76	0.052	-0.569	0.450	-0.600
	N7H···O2 (T2)	4	14.67	0.050	-0.467	0.460	-0.638

Note: [a] Number of times a particular H-bond occurs in a structure; [b] Stabilization energy for the LP→BD* interaction (defined by formula (3) in the manuscript), where the LP – lone pair(s) of the H-bond acceptor atom, BD* is the anti-bonding orbital of the H-bond donating group; [c] Charge transfer to the anti-bonding orbital corresponding to the H-bond donor group; [d] Natural charges of the donor (A), hydrogen (H), and acceptor (B) atoms involved in the H-bond AH···B.
Notations T1 and T2 refer to different tetrads in the $(B4)_2$ complexes.

Table S6. Parameters and energies of the H-bonds and ion-base coordination contacts at the B3LYP-D/6-31++G(d,p) level of theory. The geometries were optimized in Gaussian 09. QTAIM and the NBO analyses were performed in the AIMAll and Gaussian 09 programs, using BLYP-D/6-31++G(d,p) wavefunctions and geometries. All characteristics are calculated as average values for each type of non-covalent contact.

Complex	Interaction	N[a]	ρ[b]	Δρ[b]	E_{HB}[c]	$d_{A...B}$[d]	$d_{H...B}$[e]	AHB[f]	E_2[g]	C_{ij}[h]
G4·Na^+	N1H...O6	4	0.033	0.099	7.66	2.83	1.82	166.0	21.24	2.681
	N2H...N7	4	0.036	0.089	7.35	2.89	1.86	172.2	23.69	2.820
	O6...Na^+	4	0.020	0.121	-	2.32	-	-	-	2.236
G4·K^+	N1H...O6	4	0.028	0.087	6.57	2.90	1.87	175.3	16.94	3.822
	N2H...N7	4	0.023	0.058	4.57	3.04	2.05	164.4	12.38	7.476
	O6...K^+	4	0.023	0.105	-	2.59	-	-	-	2.381
X4·Na^+	N1H···O6	4	0.038	0.117	8.90	2.78	1.76	166.0	25.27	2.780
	N7H···O2	4	0.035	0.107	7.99	2.82	1.79	175.0	24.31	4.180
	O6...Na^+	4	0.017	0.104	-	2.37	-	-	-	3.083
X4·K^+	N1H···O6	4	0.036	0.111	8.40	2.80	1.78	167.0	24.14	3.108
	N7H···O2	4	0.036	0.109	8.12	2.81	1.78	175.3	24.30	4.037
	O6...K^+	4	0.014	0.061	-	2.79	-	-	-	5.604

Note: [a] Number of times a particular interaction occurs in a structure; [b] The electron density and the Laplacian of electron density values at the bond critical point (3,-1), a.u.; [c] The H-bond energy calculated by the EML formula (4), kcal/mol; [d] The distance between atoms A and B in the case of the hydrogen bond AH···B, Å. For ion-base contacts, this is the distance between the O6 atom of Gua/Xan and the metal ion; [e] The distance between the hydrogen (H) and the H-bond acceptor atom (B), Å; [f] The H-bond angle AH···B, degrees; [g] The stabilization energy for the LP→BD^* interaction (defined by formula (3) in the manuscript), where the LP – lone pair(s) of the H-bond acceptor atom, BD^* is the anti-bonding orbital of the H-bond donating group, kcal/mol; [h] Compliance constant, Å/mDyn.

Table S7. NPA charges calculated for atoms A and B, involved in van der Waals contacts A···B in $(B4)_2$ complexes. All characteristics are calculated as average values for each type of van der Waals contact.

Complex	Interaction	N[a]	Q_A	Q_B
$(G4)_2$	C2 ···C5	4	0.552	-0.093
	N3···N7	4	-0.532	-0.471
	N2···N7	4	-0.752	-0.469
	N2···C4	1	-0.760	0.316
	O6···N1	4	-0.660	-0.565
$(G4)_2$ (planar)	O6···N1	4	-0.564	-0.658
	N2···C4	4	-0.759	0.317
	N2···N7	3	-0.757	-0.469
	N3 ···N2	1	-0.469	-0.757
	N3···N7	4	-0.531	-0.472
	C2···C5	4	0.556	-0.091
$(G4)_2{\cdot}Na^+$ (fully optimized)	O6···N1	8	-0.668	-0.557
	O6···O6	8	-0.658	-0.668
	N2···C5	8	-0.755	-0.085
	C2···N7	8	0.556	-0.471
$(G4)_2{\cdot}Na^+$ (planar)	C2···N7	4	0.555	-0.470
	N2···C5	8	-0.756	-0.084
	O6···N1	8	-0.557	-0.662
	N3···N7	4	-0.526	-0.471
$(G4)_2{\cdot}K^+$	O6···N1	4	-0.606	-0.546
	N2···C5	8	-0.752	-0.078
	C2···N7	8	0.555	-0.470
$(X4)_2$	O2···N3	4	-0.660	-0.517
	N3···C5	4	-0.528	-0.070
	N1···C6	4	-0.581	0.583
	N3···N7	4	-0.528	-0.464
	N7···O2	4	-0.458	-0.655
$(X4)_2$ (planar)	C2···C5	4	0.721	-0.564
	O6···N1	4	-0.624	-0.656
	N3···N7	4	-0.527	-0.578
	N7···O2	4	-0.455	-0.524
	O2···N3	3	-0.659	-0.656
	O6···N3	1	-0.660	-0.464
$(X4)_2{\cdot}Na^+$ (fully optimized)	O6···N1	7	-0.632	-0.572
	O2···N3	3	-0.651	-0.512
	C2···C5	3	0.722	-0.066
	N3···N7	4	-0.522	-0.463
	N1···C6	4	-0.572	0.583
	O6···O6	3	-0.632	-0.632
$(X4)_2{\cdot}Na^+$ (planar)	C2···C5	4	0.723	-0.065
	N1···C6	4	-0.574	0.585
	O6···N1	4	-0.642	-0.568
	N3···N7	4	-0.522	-0.464
	N7···O2	4	-0.455	-0.648
	O6···O6	4	-0.642	-0.638
$(X4)_2{\cdot}K^+$	O2···N3	4	-0.642	-0.514

Complex	Interaction	N[a]	Q_A	Q_B
	N3···C5	4	-0.527	-0.068
	N1···C6	2	-0.569	0.578
	N1···C5	2	-0.569	0.579
	C4···N7	4	0.306	-0.467
	N7···O2	4	-0.461	-0.638

Note: [a] Number of times a particular van der Waals contact occurs in a structure.