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SUPPLEMENTARY MATERIALS

The influence of phosphorothioate on charge migration in single and double stranded DNA. A theoretical approach.

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Table 1SM. Dihedral angels α (O3'-P-O5'-C5'), ξ (C3'-O3' -P-O5') in [°] and hydrogen bonds lengths in [Å] of d[$G_{PX}G$] and [$G_{PX}G$]*[$C_{PO}C$] (X= O or S) systems in their neutral, radical cation and radical anion forms

Selected dihedral angels [°]						
System	**d[$G_{PX}G$]**		**d[$G_{PX}G$]*d[$C_{PO}C$]**			
			d[$G_{PX}G$]		**d[$C_{PO}C$]**	
	C3'-O3' -P-O5'	**O3'-P-O5'-C5'**	**C3'-O3' -P-O5'**	**O3'-P-O5'-C5'**	**C3'-O3' -P-O5'**	**O3'-P-O5'-C5'**
NEUTRAL						
PO X=O	-90.54	-71.71	-164.83	-42.45	-172.14	-29.92
[S_P] X=S	-119.06	-46.44	-161.95	-43.87	-172.21	-30.11
[R_P] X=S	-75.91	-86.27	-159.75	-83.62	-174.52	-31.02
Radical CATION						
PO X=O	-102.20	-64.39	-152.38	-37.91	-177.09	-39.19
[S_P] X=S	-133.37	-47.59	-68.77	-62.29	-178.31	-38.92
[R_P] X=S	171.92	-95.35	-160.42	-90.48	-172.59	-36.06
Radical ANION						
PO X=O	213.15	-47.52	-175.72	-45.05	-164.00	-24.37
[S_P] X=S	-128.99	15.15	-61.05	-62.02	-166.03	-24.49
[R_P] X=S	-79.92	-79.90	-156.99	-83.80	-171.00	35.29
Hydrogen bonds length [Å]						
System	**d[$G_{PX}G$]*d[$C_{PO}C$]**					
	$^{5'}$G:::C$^{3'}$			**$^{3'}$G:::C$^{5'}$**		
	O6--N4 (HB1)	**N1--N3 (HB2)**	**N2--O2 (HB3)**	**O6--N4 (HB1)**	**N1--N3 (HB2)**	**N2--O2 (HB3)**
Ref.	2.92/3.00	2.92/3.00	2.79/2.87			
NEUTRAL						
PO X=O	2.780	2.888	2.993	2.830	2.913	2.918
[S_P] X=S	2.781	2.890	2.992	2.830	2.912	2.915
[R_P] X=S	2.777	2.887	2.999	2.854	2.921	2.909
Radical CATION						
PO X=O	2.828	2.860	2.952	2.976	2.793	2.669
[S_P] X=S	2.825	2.859	2.969	2.991	2.801	2.657
[R_P] X=S	2.827	2.877	2.894	2.941	2.813	2.692
Radical ANION						
PO X=O	2.973	2.798	2.767	2.872	2.874	2.947
[S_P] X=S	2.958	2.770	2.804	2.915	2.878	2.916
[R_P] X=S	2.982	2.779	2.781	2.893	2.860	2.971

Ref.: W.K. Olson, M. Bansal, S.K. Burley, R.E. Dickerson, M.Gerstein, S.C. Harvey, U. Heinemann, X-J. Lu, S. Neidle, Z. Shakked,H. Sklenar, M. Suzuki, C-S Tung, E. Westhof, C. Wolberger, H.M. Berman, J. Mol. Biol., 2001, **313**, 229

Table 2SM. The differences in hydrogen bonds length in [R_P] d[G_{PS}G]*[C_{PO}C], [S_P] d[G_{PS}G]*[C_{PO}C] and d[G_{PO}G]*[C_{PO}C], between their suitable neutral form and radical anion or cation ones, given in [**Å**]

d[G_{PX}G]*[C_{PO}C]						
Hydrogen bonds length differences in [Å]						
System	$^{3'}$G:::C$^{5'}$			$^{5'}$G:::C$^{3'}$		
	HB1	HB2	HB3	HB1	HB2	HB3
	Radical Cation					
PO X=O	-0.146	0.12	0.249	-0.048	0.028	0.041
[R_P] X=S	-0.161	0.111	0.258	-0.044	0.031	0.023
[S_P] X=S	-0.087	0.108	0.217	-0.05	0.01	0.015
	Radical Anion					
PO X=O	-0.042	0.039	-0.029	-0.193	0.09	0.226
[R_P] X=S	-0.085	0.034	-0.001	-0.177	0.12	0.188
[S_P] X=S	-0.039	0.061	-0.062	-0.205	0.108	0.218

Table 3SM. Charge, dipole moment and selected distances of d[$G_{PX}G$] (X= O or S) systems in their neutral, radical cation and radical anion forms.

Charge distribution in [au] an dipile moment in [D]						
d[$G_{PX}G$]						
System	3'-sugar	3'-guanine	5'-sugar	5'-guanine	$HXPO_3$	DM
NEUTRAL						
PO X=O	0.3158	-0.1055	0.2395	-0.2120	-0.2384	11.41
[R_P] X=S	0.3209	-0.1082	0.2580	-0.2079	-0.2625	8.01
[S_P] X=S	0.3159	-0.0997	0.2486	-0.2033	-0.2608	11.82
Radical CATION						
PO X=O	0.3773	-0.0611	0.3720	0.5925	-0.2808	8.56
[R_P] X=S	0.2994	-0.0153	0.2688	0.6777	-0.2307	7.38
[S_P] X=S	0.3278	-0.0154	0.3660	0.6081	-0.2867	8.25
Radical ANION						
PO X=O	-0.5846	-0.0602	-0.1680	-0.0106	-0.1770	18.41
[R_P] X=S	0.1274	-0.1675	0.1017	-0.2146	-0.8478	11.52
[S_P] X=S	0.1292	-0.0781	0.0637	-0.2584	-0.8559	15.15
Selected bonds distances in [Å]						
PO X=O	O5'-P	C1'-N9	O3'-P	C1'-N9		
Neutral	1.590	1.452	1.597	1.435		
Cation	1.601	1.457	1.601	1.450		
Anion	1.608	1.452	1.617	1.454		
[R_P] X=S						
Neutral	1.612	1.452	1.594	1.435		
Cation	1.605	1.451	1.608	1.455		
Anion	1.691	1.454	1.688	1.450		
[S_P] X=S						
Neutral	1.608	1.445	1.595	1.433		
Cation	1.600	1.451	1.613	1.460		
Anion	1.717	1.448	1.672	1.469		

Table 4 5 SM. Atomic charge [au], dipole moment [D] and selected distances [Å] of d[$G_{PX}G$]*[$C_{PO}C$] X= O or S systems in their neutral, radical cation and radical anion forms.

Charge distribution in [au] an dipile moment in [D]											
d[$G_{PX}G$]*[$C_{PO}C$]											
System	**3'-sugar**	**3'-guanine**	**5'-sugar**	**5'-guanine**	**O=P-XH**	**3'-cytozine**	**3'-sugar**	**5'-sugar**	**5'-cytozine**	**O=P-OH**	**DM**
	NEUTRAL										
PO X=O	0.2140	-0.1843	0.2074	-0.1800	-0.2610	0.0028	0.2472	0.1761	0.0255	-0.2499	9.64
[R_P] X=S	0.2341	-0.1716	0.1902	-0.1737	-0.2788	0.0038	0.2506	0.1752	0.0259	-0.2496	10.57
[S_P] X=S	0.2165	-0.1817	0.2168	-0.1814	-0.2677	-0.0060	0.2617	0.1956	0.0160	-0.2719	10.35
	Radical CATION										
PO X=O	0.3035	0.4016	0.2435	-0.1567	-0.2248	0.0409	0.2707	0.2150	0.1373	-0.2317	6.05
[R_P] X=S	0.3256	0.3891	0.2222	-0.1084	-0.2473	0.0355	0.2847	0.2321	0.1181	-0.2515	7.16
[S_P] X=S	0.2944	0.3735	0.2871	-0.1771	-0.2105	0.0391	0.2717	0.2154	0.1382	-0.2318	5.32
	Radical ANION										
PO X=O	0.2103	-0.1936	0.1746	-0.2894	-0.3025	-0.5250	0.1470	0.1562	-0.0654	-0.3139	11.52
[R_P] X=S	0.2246	-0.2050	0.1637	-0.2948	-0.2899	-0.5268	0.1521	0.1430	-0.0575	-0.31053	10.49
[S_P] X=S	0.1768	-0.2397	0,2016	-0.2727	-0.2585	-0.5343	0.1458	0.1574	-0.0537	-0.31290	8.45
Selected bonds distances in [Å]											
PO X=O	O5'-P	C1'-N9	O3'-P	C1'-N9		O5'-P	C1'-N1	O3'-P	C1'-N1		
Neutral	1.594	1.439	1.584	1.438		1.591	1.451	1.587	1.443		
Cation	1.597	1.462	1.587	1.443		1.594	1.458	1.591	1.453		
Anion	1.591	1.433	1.581	1.430		1.589	1.421	1.586	1.442		
[R_P] X=S											
Neutral	1.605	1.438	1.593	1.436		1.592	1.451	1.588	1.443		
Cation	1.614	1.460	1.600	1.437		1.593	1.457	1.591	1.453		
Anion	1.603	1.432	1.591	1.428		1.591	1.421	1.590	1.443		
[S_P] X=S											
Neutral	1.597	1.439	1.591	1.438		1.592	1.451	1.588	1.443		
Cation	1.611	1.473	1.587	1.450		1.593	1.459	1.591	1.454		
Anion	1.596	1.445	1.589	1.444		1.590	1.423	1.585	1.443		

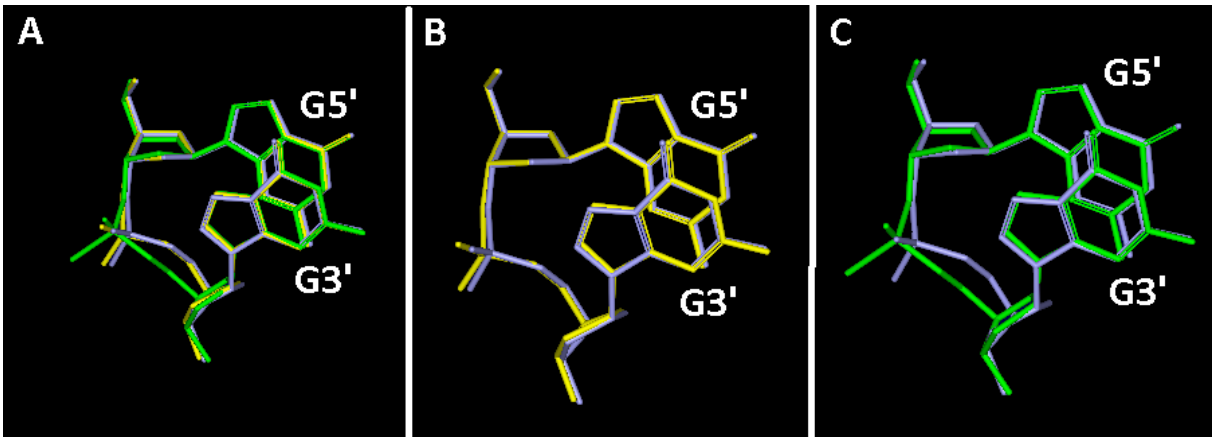

Figure 1SM. Visualisation of spatial geometry comparison of **d[G_{PO}G]** (gray), **[S_P] d[G_{PS}G]** (green) and **[R_P] d[G_{PS}G]** (yellow) in their neural forms, optimized at M06-2X/6-31+G** level of theory. **G3′** -3′ -end guanie, **G5′** – 5′-end guanie.

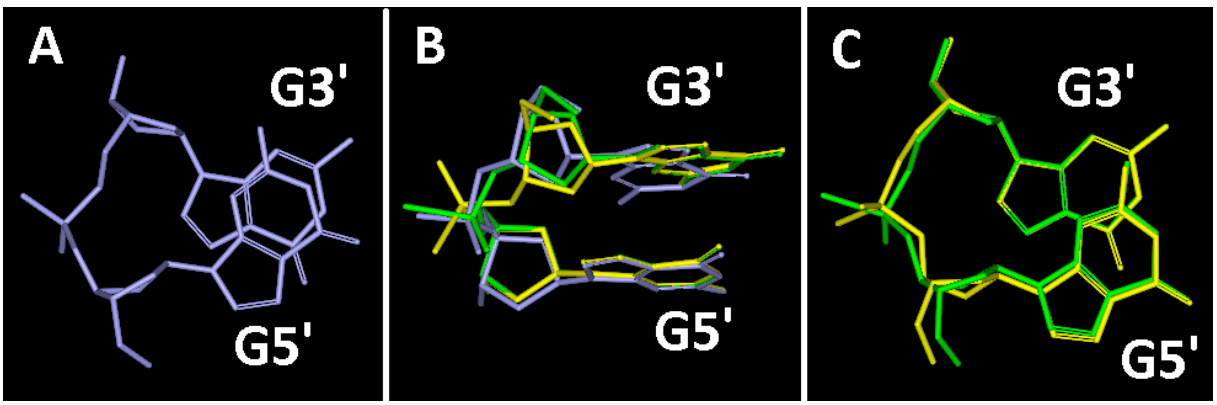

Figure 2SM. Visualisation of spatial geometry comparison of **d[G_{PO}G]** (gray), **[S_P] d[G_{PS}G]** (violet) and **[R_P] d[G_{PS}G]** (yellow) in their radical cation forms, optimized at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie.

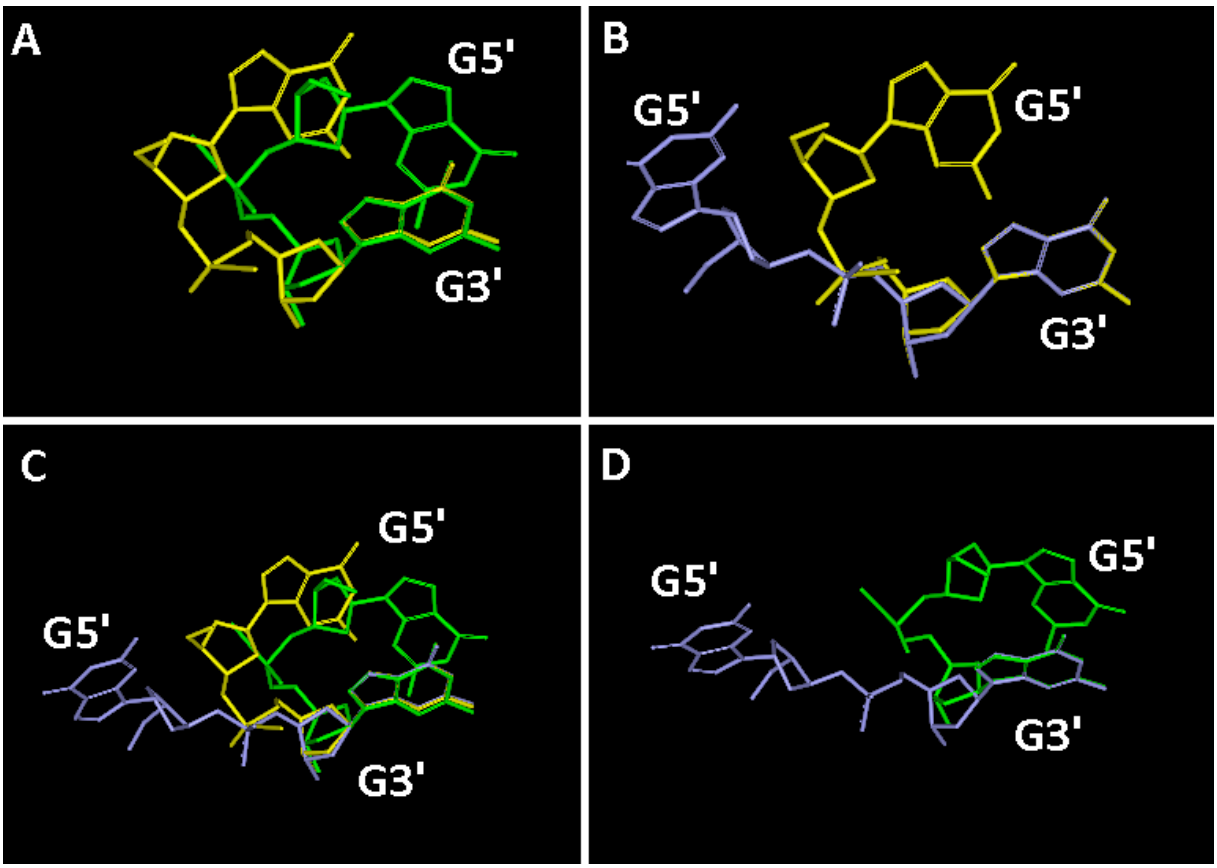

Figure 3SM. Visualisation of spatial geometry comparison of **d[G_{PO}G]** (violet), **[S_P] d[G_{PS}G]** (green) and **[R_P] d[G_{PS}G]** (yellow) in their radical anion forms, optimized at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie.

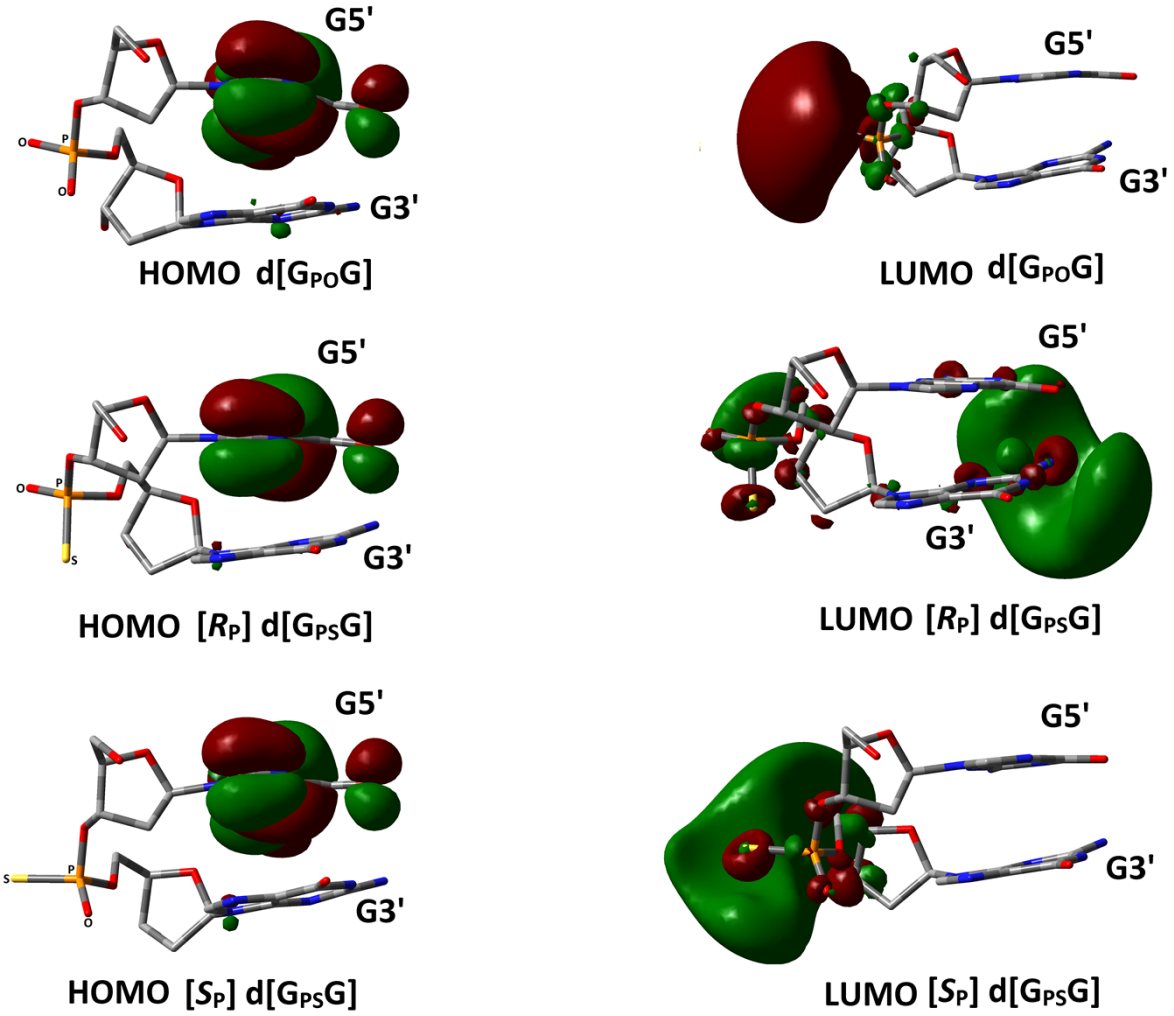

Figure 4SM. HOMO and LUMO visualisation in neutral forms of **d[G_{PO}G]**, **[S_P] d[G_{PS}G]** and **[R_P] d[G_{PS}G]**, calculated at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie.

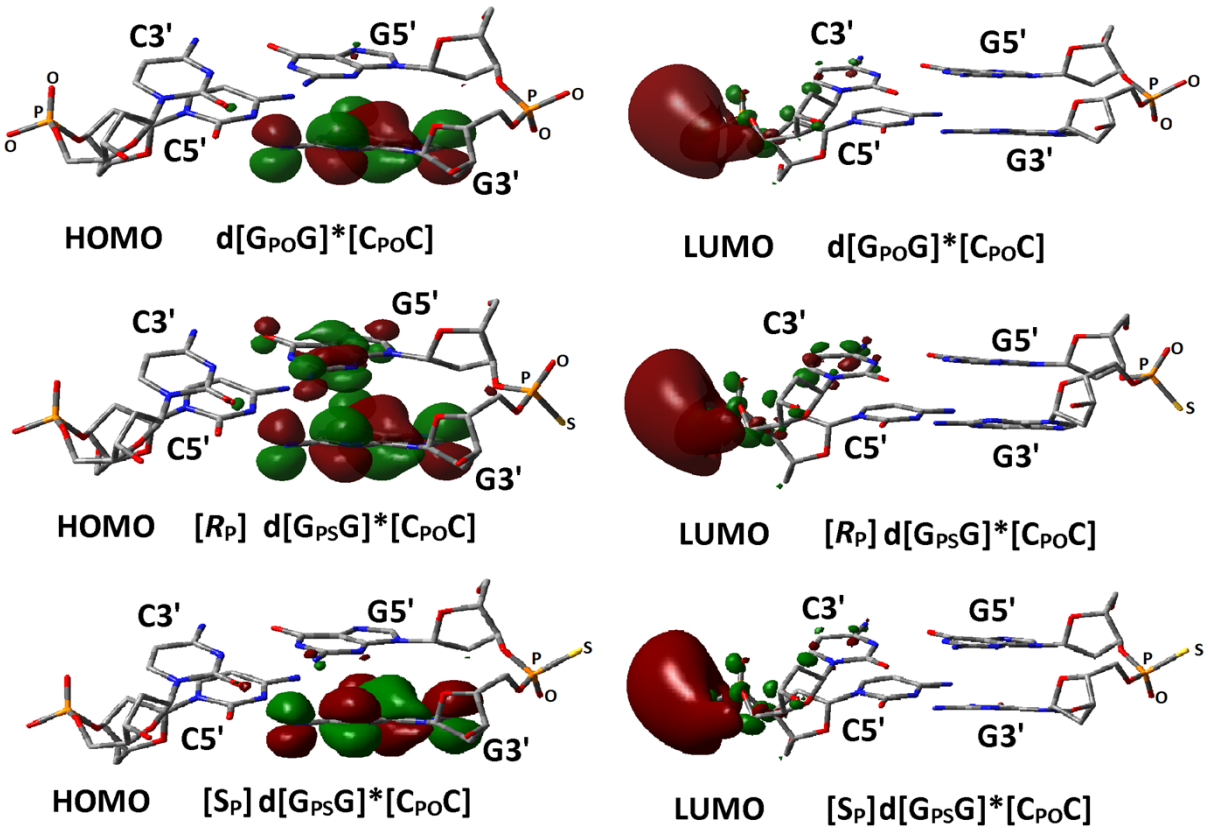

Figure 5SM. HOMO and LUMO visualisation in neutral forms of **d[G_{PO}G]*d[C_{PO}C]**, **[S_P] d[G_{PS}G]*d[C_{PO}C]** and **[R_P] d[G_{PS}G]*d[C_{PO}C],** calculated at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie, **C3′** – 3′-end cytosine, **C5′** – 5′-end cytosine.

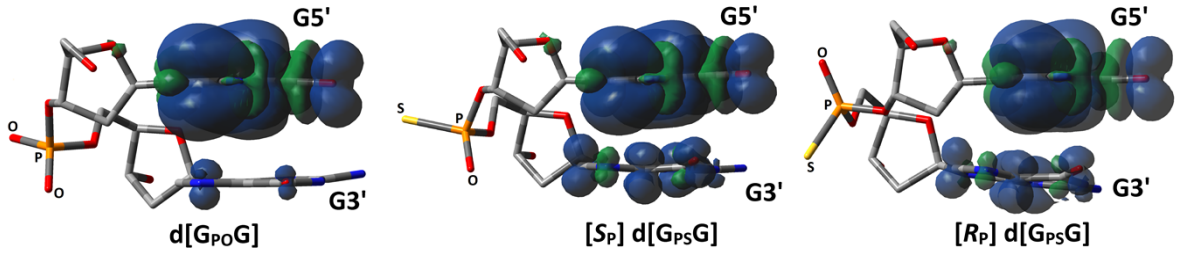

Figure 6SM. Hirshfeild spin density distribution, summed into heavy atoms, visualisation of radical cation forms of **d[G$_{PO}$G]**, **[S$_P$] d[G$_{PS}$G]** and **[R$_P$] d[G$_{PS}$G]**, calculated at M06-2X/6-31+G** level of theory. **G3**′ -3′ -end guanie, **G5**′ – 5′-end guanie.

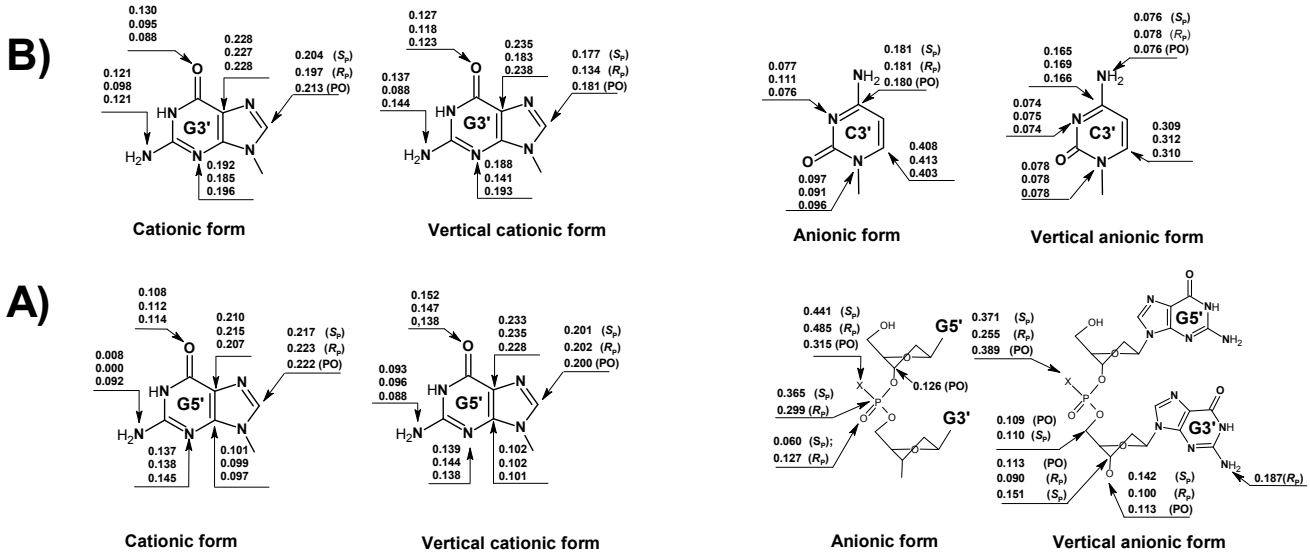

Figure 7SM. Hirshfield atomic spin density distribution, summed into heavy atoms, calculated at M06-2X/6-31+G** level of theory. **A)** spin distribution on **d[G$_{PX}$G]** molecules (X=O or S), **B)** spin distribution on **d[G$_{PX}$G]*[C$_{PO}$G]** (X=O or S)**. PO** – phosphate internucleotide bond, ***R*$_P$** – R; ***S*$_P$** - S diasteromer of phosphorothioate internucleotide bond, **G3'** – 3'-end guanine, **C3'** – 3'-end cytosine, **C5'** – 5-end cytosine, **G5'** – 5'-end guanine.

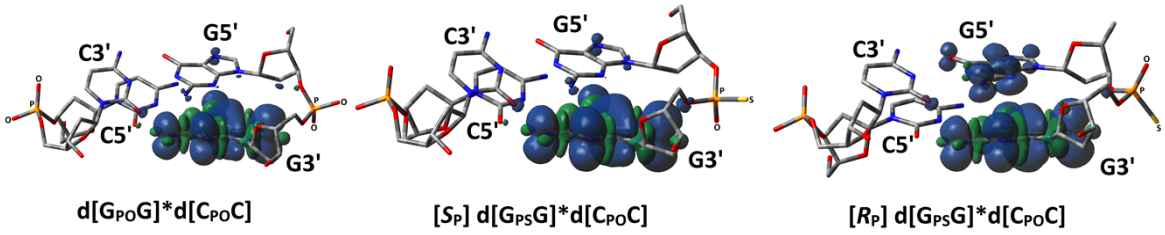

Figure 8SM. Hirshfeild spin density distribution, summed into heavy atoms, visualisation of radical cation forms of **d[G_{PO}G]*d[C_{PO}C]**, **[S_P] d[G_{PS}G]*d[C_{PO}C]** and **[R_P] d[G_{PS}G]*d[C_{PO}C]**, calculated at M06-2X/6-31+G** level of theory. **G3**′ – 3′ -end guanie, **G5**′ – 5′-end guanie, **C3**′ – 3′ -end cytosine, **C5**′ – 5′-end cytosine.

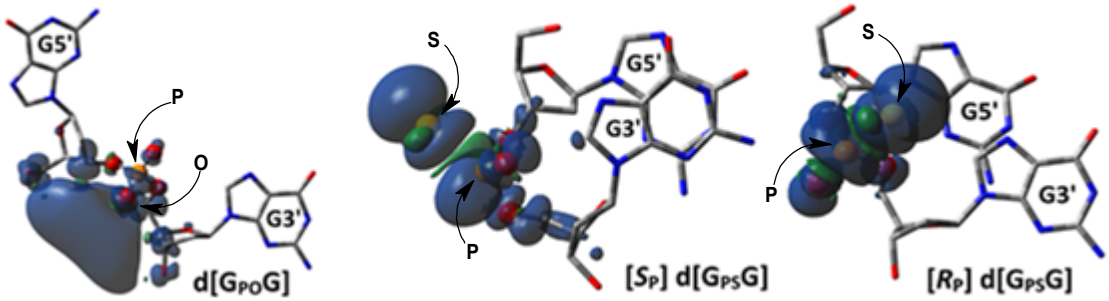

Figure 9SM The Hirshfeild spin density visualisation of radical anion forms of **d[G_{PO}G]**, **[S_P] d[G_{PS}G]** and **[R_P] d[G_{PS}G]**,calculated at M06-2X/6-31+G** level of theory. **G3**′ -3′ -end guanie, **G5**′ – 5′-end guanie.

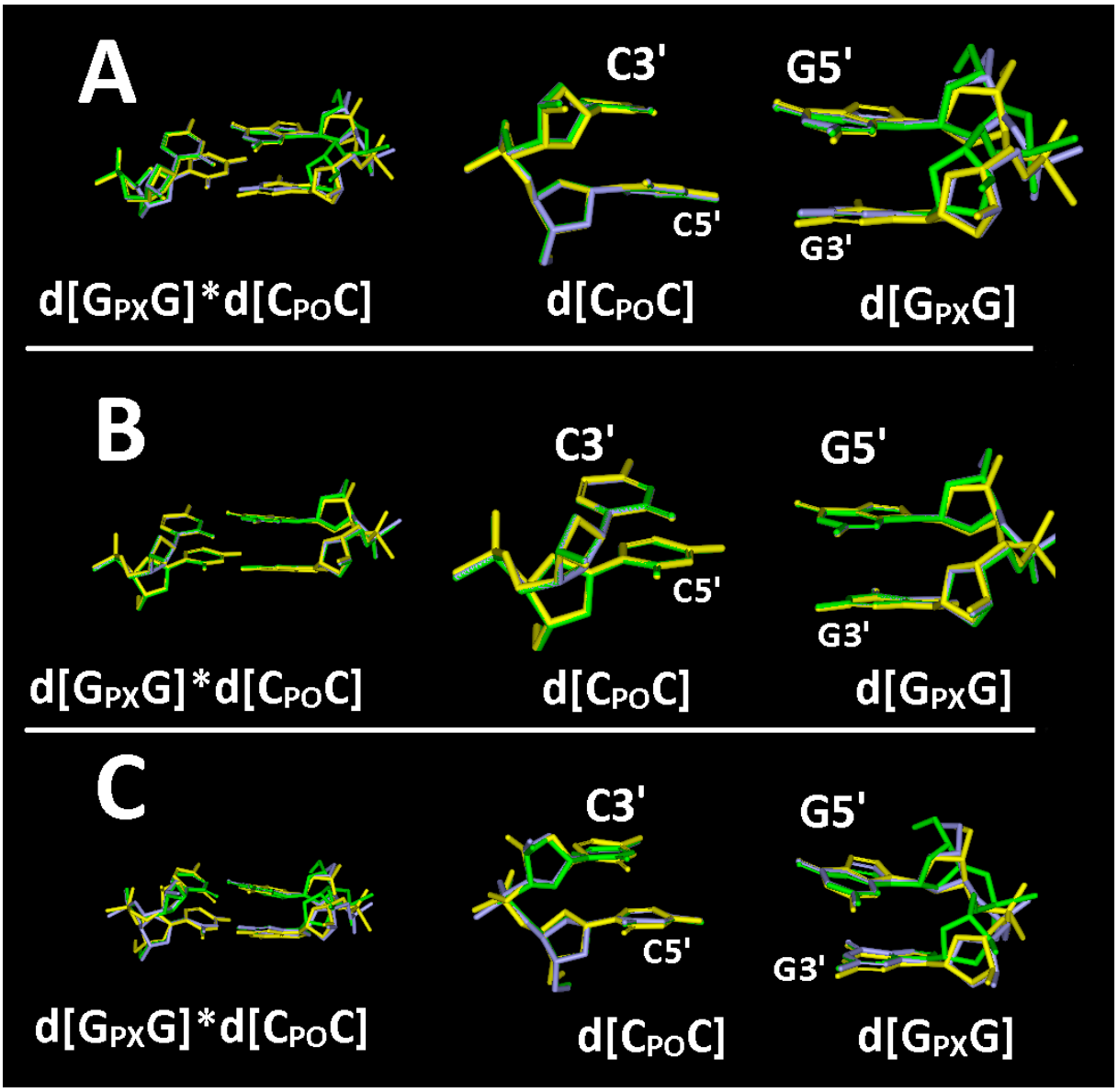

Figure 10SM. Visualisation of spatial geometry comparison of **d[G_{PO}G]*d[C_{PO}C]** (violet, X=O), **[S_P] d[G_{PS}G]*d[C_{PO}C]** (green, X=S) and **[R_P] d[G_{PS}G]*d[C_{PO}C]** (yellow, X=S), in their: radical A) cation, C) anion and B) neutral forms, optimized at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie, **C3′** – 3′-end cytosine, **C5′** – 5′-end cytosine.

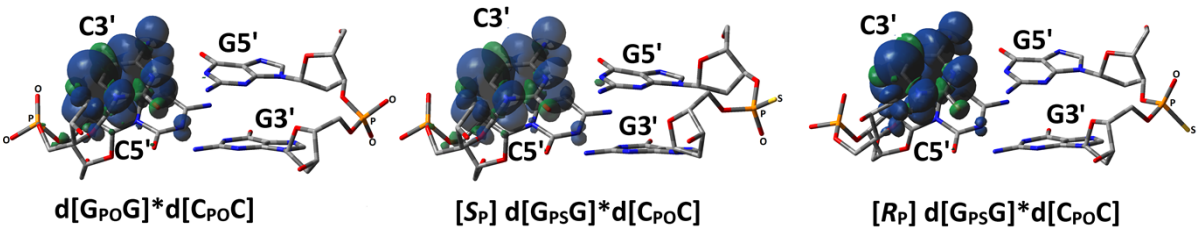

Figure 11SM. Hirshfeild spin density distribution, summed into heavy atoms, visualisation of radical anion forms of **d[G_{PO}G]*d[C_{PO}C]**, **[S_P] d[G_{PS}G]*d[C_{PO}C]** and **[R_P] d[G_{PS}G]*d[C_{PO}C]**, calculated at M06-2X/6-31+G** level of theory. **G3′** – 3′-end guanie, **G5′** – 5′-end guanie, **C3′** – 3′-end cytosine, **C5′** – 5′-end cytosine.