SUPPLEMENTARY MATERIALS

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

B.T. Karwowski
### Table 1SM. Dihedral angels $\alpha$ (O3'-P-O5'-C5'), $\xi$ (C3'-O3' -P-O5') in [°] and hydrogen bonds lengths in [Å] of d[GpG] and [GpG][CpC] (X= O or S) systems in their neutral, radical cation and radical anion forms

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<tr>
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<td>C3'-O3' -P-O5'</td>
<td>O3'-P-O5'-C5'</td>
<td>C3'-O3' -P-O5'</td>
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<td>-79.90</td>
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<td>[SP] X=S</td>
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<td>[SP] X=S</td>
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<td>[RP] X=S</td>
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Table 2SM. The differences in hydrogen bonds length in $[\mathcal{R}_P] \ d[G_{PS}G]^*[C_{PS}C]$, $[\mathcal{S}_P] \ d[G_{PS}G]^*[C_{PS}C]$ and $d[G_{PS}G]^*[C_{PS}C]$, between their suitable neutral form and radical anion or cation ones, given in $[\text{Å}]$.

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<th>System</th>
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<tr>
<td></td>
<td>HB1</td>
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<tr>
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<td>0.034</td>
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<tr>
<td>$[\mathcal{S}_P] X=S$</td>
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Table 3SM. Charge, dipole moment and selected distances of d[GxG] (X= O or S) systems in their neutral, radical cation and radical anion forms.

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<th>System</th>
<th>3'-sugar</th>
<th>3'-guanine</th>
<th>5'-sugar</th>
<th>5'-guanine</th>
<th>HXPO₃</th>
<th>DM</th>
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<td></td>
</tr>
<tr>
<td>PO X=O</td>
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<td>0.2395</td>
<td>-0.2120</td>
<td>-0.2384</td>
<td>11.41</td>
</tr>
<tr>
<td>[Rₓ] X=S</td>
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<td>-0.1082</td>
<td>0.2580</td>
<td>-0.2079</td>
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<tr>
<td>[Sₓ] X=S</td>
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<td>0.2486</td>
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<td>-0.2608</td>
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</tr>
<tr>
<td>Radical CATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>[Rₓ] X=S</td>
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<td>0.2688</td>
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<td>-0.2307</td>
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<td>[Sₓ] X=S</td>
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<td>0.3660</td>
<td>0.6081</td>
<td>-0.2867</td>
<td>8.25</td>
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<tr>
<td>Radical ANION</td>
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<tr>
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Selected bonds distances in Å:

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<th>O3'-P</th>
<th>C1'-N9</th>
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<td>1.597</td>
<td>1.435</td>
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<tr>
<td>Cation</td>
<td>1.601</td>
<td>1.457</td>
<td>1.601</td>
<td>1.450</td>
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<tr>
<td>Anion</td>
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<td>1.452</td>
<td>1.617</td>
<td>1.454</td>
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<tr>
<td>[Rₓ] X=S</td>
<td>1.612</td>
<td>1.452</td>
<td>1.594</td>
<td>1.435</td>
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<tr>
<td>Cation</td>
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<td>1.451</td>
<td>1.608</td>
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<tr>
<td>Anion</td>
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<td>1.454</td>
<td>1.688</td>
<td>1.450</td>
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<tr>
<td>[Sₓ] X=S</td>
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<td>1.445</td>
<td>1.595</td>
<td>1.433</td>
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<tr>
<td>Cation</td>
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<td>1.451</td>
<td>1.613</td>
<td>1.460</td>
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<tr>
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<td>1.672</td>
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Table 4 SM. Atomic charge [au], dipole moment [D] and selected distances [Å] of d(GpXG)*[CpXC] \(X=O\) or S systems in their neutral, radical cation and radical anion forms.

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<tr>
<th>System</th>
<th>(3')-sugar</th>
<th>(3')-guanine</th>
<th>(5')-sugar</th>
<th>(5')-guanine</th>
<th>(\text{O=PH})</th>
<th>(3')-cytosine</th>
<th>(5')-sugar</th>
<th>(5')-cytosine</th>
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<td>0.1761</td>
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<tr>
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<td>0.1902</td>
<td>-0.1737</td>
<td>-0.2788</td>
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<td>-0.1814</td>
<td>-0.2677</td>
<td>-0.0060</td>
<td>0.2617</td>
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<td>0.0160</td>
<td>-0.2719</td>
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<tr>
<td><strong>Radical CATION</strong></td>
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<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
<td> </td>
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</tr>
<tr>
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<td>-0.2473</td>
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<td>0.2321</td>
<td>0.1181</td>
<td>-0.2515</td>
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<tr>
<td>([\text{SP}] X=S)</td>
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<td> </td>
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<td> </td>
<td> </td>
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**Selected bonds distances in [Å]**

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<td>1.587</td>
<td>1.443</td>
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<td>1.458</td>
<td>1.591</td>
<td>1.453</td>
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<td>1.592</td>
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<td><strong>S_{p} X=S</strong></td>
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<th>(\text{C1'-N9})</th>
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<th>(\text{C1'-N1})</th>
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<td>1.592</td>
<td>1.451</td>
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<tr>
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<td>1.589</td>
<td>1.444</td>
<td>1.590</td>
<td>1.423</td>
<td>1.585</td>
<td>1.443</td>
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</table>
**Figure 1SM.** Visualisation of spatial geometry comparison of \( d[G_5G] \) (gray), \( [S_5] d[G_5G] \) (green) and \( [R_5] d[G_5G] \) (yellow) in their neural forms, optimized at M06-2X/6-31+G** level of theory. \( G_{3\prime} - 3\prime\)-end guanine, \( G_{5\prime} - 5\prime\)-end guanine.

**Figure 2SM.** Visualisation of spatial geometry comparison of \( d[G_5G] \) (gray), \( [S_5] d[G_5G] \) (violet) and \( [R_5] d[G_5G] \) (yellow) in their radical cation forms, optimized at M06-2X/6-31+G** level of theory. \( G_{3\prime} - 3\prime\)-end guanine, \( G_{5\prime} - 5\prime\)-end guanine.
Figure 3S. Visualisation of spatial geometry comparison of dG5G (violet), [S] dG5G (green) and [R] dG5G (yellow) in their radical anion forms, optimized at M06-2X/6-31+G** level of theory. G3’ – 3’-end guanine, G5’ – 5’-end guanine.
Figure 4SM. HOMO and LUMO visualisation in neutral forms of d[G₆₃G], {SP} d[G₆₅G] and {RP} d[G₆₅G], calculated at M06-2X/6-31+G** level of theory. G₃₈ – 3₈-end guanie, G₅₅ – 5₅-end guanie.
Figure S5M. 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 guanine, G5′ – 5′-end guanine, C3′ – 3′-end cytosine, C5′ – 5′-end cytosine.
**Figure 6SM.** Hirshfield spin density distribution, summed into heavy atoms, visualisation of radical cation forms of d(GpG), [S_p] d(GpG) and [R_p] d(GpG), calculated at M06-2X/6-31+G** level of theory. G38'-38'-end guanine, G58'–58'-end guanine.

**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(GpG) molecules (X=O or S), B) spin distribution on d(GpG) [S_p] d(GpG) (X=O or S), PO – phosphate internucleotide bond, R_p – 5 diasteromer of phosphorothioate internucleotide bond, G38' – 3'-end guanine, C3' – 3'-end cytosine, C58' – 5'-end cytosine, G58' – 5'-end guanine.
Figure 8SM. Hirshfeld spin density distribution, summed into heavy atoms, visualisation of radical cation forms of \( d[GpG]d[GpC] \), \([S_p] \) \( d[GpG]d[CpC] \) and \([R_p] \) \( d[GpG]d[CpC] \), calculated at M06-2X/6-31+G** level of theory. \( G3\beta \) – 3\beta-end guanie, \( G5\beta \) – 5\beta-end guanie, \( C3\beta \) – 3\beta-end cytosine, \( C5\beta \) – 5\beta-end cytosine.

Figure 9SM. The Hirshfeld spin density visualisation of radical anion forms of \( d[GpG] \), \([S_p] \) \( d[GpG] \) and \([R_p] \) \( d[GpG] \), calculated at M06-2X/6-31+G** level of theory. \( G3\beta \) – 3\beta-end guanie, \( G5\beta \) – 5\beta-end guanie.
Figure 10SM. Visualisation of spatial geometry comparison of \(d[G_{PO}G]*d[C_{PO}C]\) (violet, \(X=O\)), \([S]\) \(d[G_{PO}G]*d[C_{PO}C]\) (green, \(X=S\)) and \([R]\) \(d[G_{PO}G]*d[C_{PO}C]\) (yellow, \(X=S\)), in their: A) radical A cation, C) anion and B) neutral forms, optimized at M06-2X/6-31+G** level of theory. \(G_{3\beta}-3\beta\)-end guanine, \(G_{5\beta}-5\beta\)-end guanine, \(C_{3\beta}-3\beta\)-end cytosine, \(C_{5\beta}-5\beta\)-end cytosine.

Figure 11SM. Hirshfeld spin density distribution, summed into heavy atoms, visualisation of radical anion forms of \(d[G_{PO}G]*d[C_{PO}C]\). [S] \(d[G_{PO}G]*d[C_{PO}C]\) and [R] \(d[G_{PO}G]*d[C_{PO}C]\), calculated at M06-2X/6-31+G** level of theory. \(G_{3\beta}-3\beta\)-end guanine, \(G_{5\beta}-5\beta\)-end guanine, \(C_{3\beta}-3\beta\)-end cytosine, \(C_{5\beta}-5\beta\)-end cytosine.