Supporting Information

Formation of S-Cl phosphorothioate adduct radicals in dsDNA-S-oligomers: Hole transfer to guanine vs. disulfide anion radical formation

by

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Table T1. HFCCs values in Gauss (G) obtained by theory and experiment. B3LYP/6-31G* method is used for the calculation.

Molecule	Radical	Atoms	HFCC (G)			
			Theory			Exp
			A_{Iso}	A_{Aniso}	Total	
DMP	-P-S$^{\div}$Cl	P	-12.31	-0.47 0.05 0.42	-12.78 -12.26 -11.89	ca. 23
		^{35}Cl	22.41	-24.25 -24.20 48.46	-1.84 -1.79 70.87	0 0 67 [a]
	[-P-S$^{\div}$S-P-]$^{-}$	P1	-8.92	-0.88 -0.27 1.15	-9.80 -9.19 -7.77	(6.0, 9.0, 7.0)
		P2	-11.33	-0.56 -0.22 0.77	-11.89 -11.56 -10.56	(16.0, 16.0, 17.0)
DIP	-P-S$^{\div}$Cl	P	-8.90	-1.32 -0.37 1.69	-10.22 -9.27 -7.21	ca. 23
		^{35}Cl	24.35	-27.01 -26.93 53.94	-2.66 -2.58 78.29	0 0 67 [b]
	[-P-S$^{\div}$S-P-]$^{-}$ [b]	P1	-9.50	-0.77 -0.20 0.97	-10.27 -9.70 -8.53	(6.0, 9.0, 7.0)
		P2	-11.70	-0.54 -0.18 0.72	-12.24 -11.88 -10.98	(16.0, 16.0, 17.0)

[a] ^{35}Cl isotope has 75% abundance.

[b] Single point calculation for [-P-S$^{\div}$S-P-]$^{-}$ of DIP obtained via substitution of the methyl group (Figure 7B in the main manuscript) by isopropyl group.

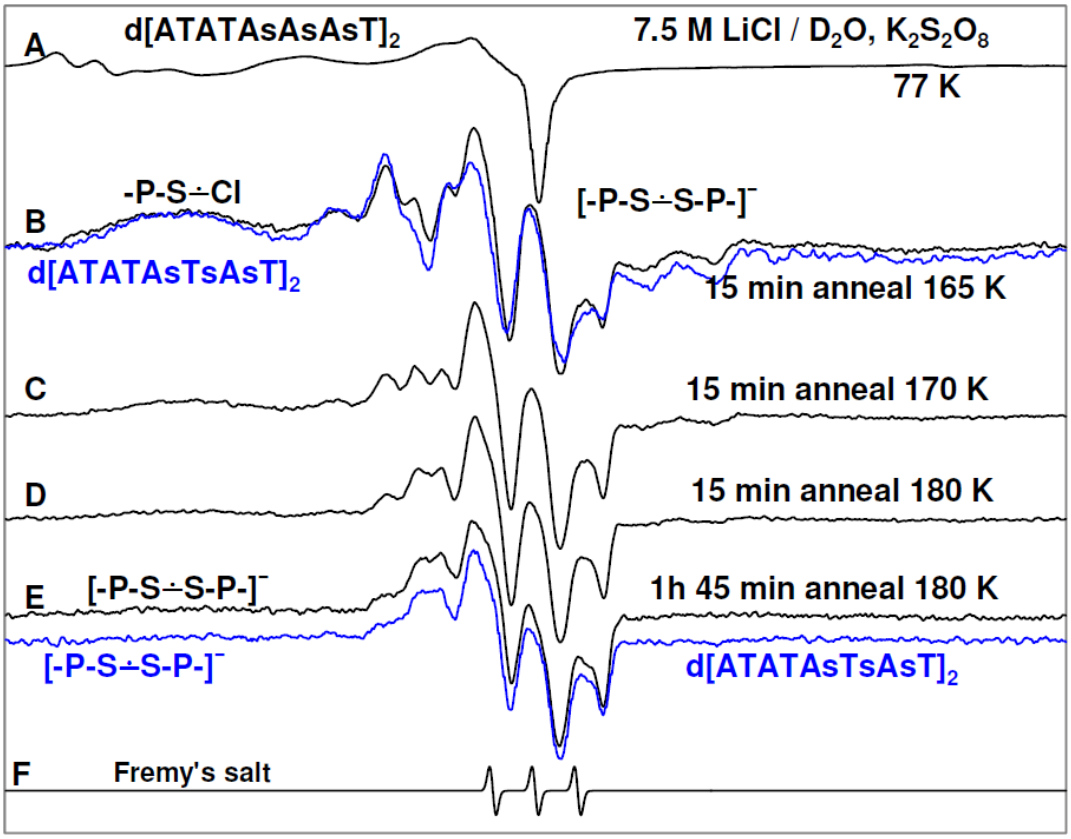

Figure S1. ESR spectra (black) of (A) γ-irradiated glassy sample of the S-oligomer containing AT mismatch d[ATATAsAsAsT]$_2$ (1.0 mg/ml in 7.5 M LiCl/D_2O) in the presence of electron scavenger $K_2S_2O_8$ (8 mg/ml) at pH ca. 5. (B-D) Spectra found after annealing to (B) 165 K for 15 min; the blue spectrum is obtained in the matched sample of the ds S-oligomer d[ATATAsTsAsT]$_2$ after annealing at 165 K for 15 min (see Figure 2C in the main manuscript). (C) 170 K for 15 min, (D) 180 K for 15 min. (E) 180 K after 1h 45 min. The blue spectrum is the isolated spectrum of [-P-S∴S-P-]$^-$ in the ds S-oligomer d[ATATAsTsAsT]$_2$ (see Figure 2E in the main manuscript).

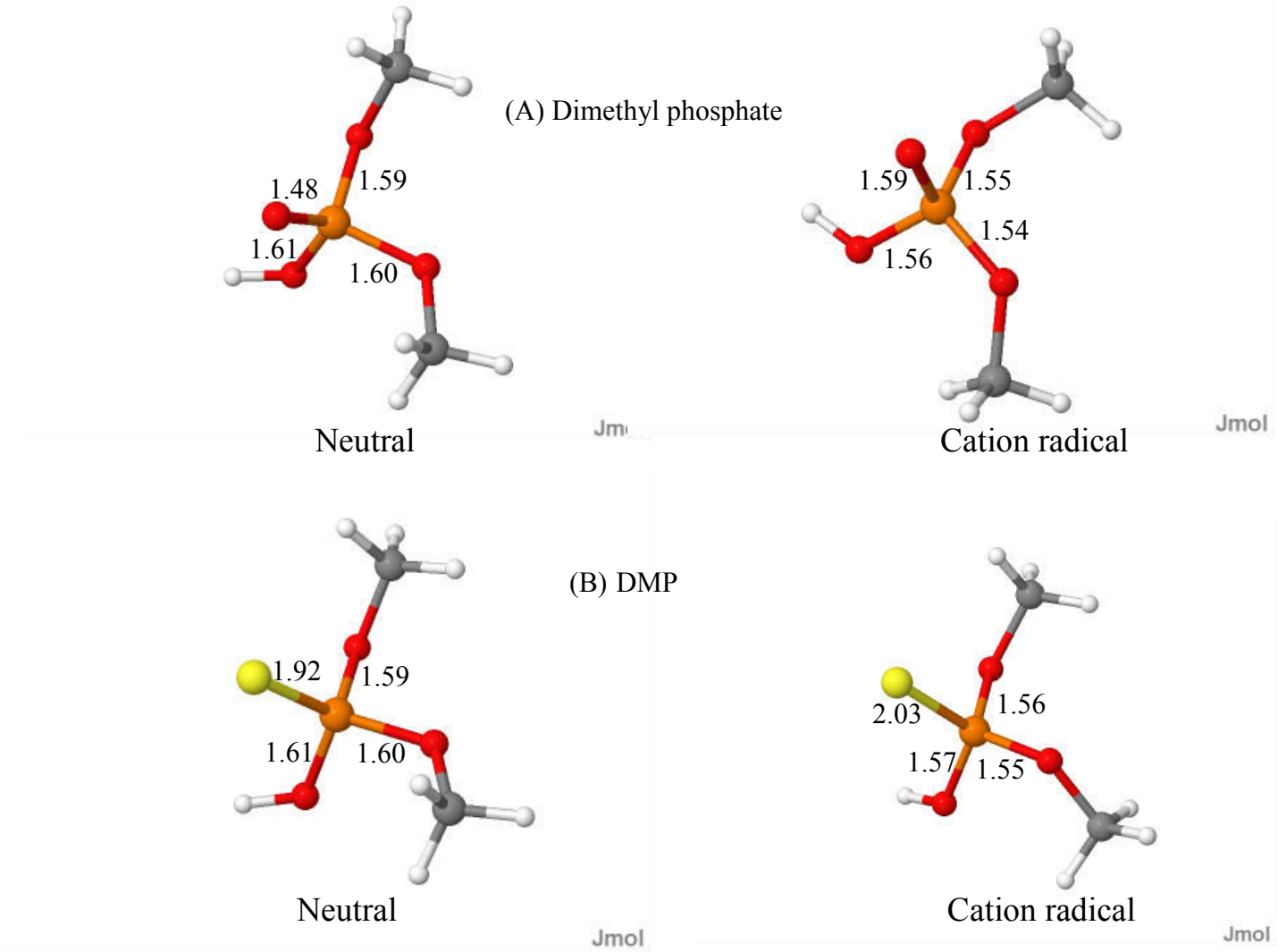

Figure S2. ωB97x/6-31++G(d) fully optimized structures of neutral parent molecule and cation radical of (A) protonated dimethyl phosphate and of (B) protonated DMP (dimethyl phosphorothioate) in the gas phase. The bond lengths are shown as well.