Impact of Arsenic/Phosphorous substitution on the intrinsic conformational properties of the phosphodiester backbone of DNA investigated using ab initio quantum mechanical calculations.

Elizabeth J. Denning and Alexander D. MacKerell Jr.*

Department of Pharmaceutical Sciences, University of Maryland, 20 Penn Street, Baltimore, MD 21201

Supporting Information

Figure S1. Upper-panel: Potential energy surfaces for the α, β, γ, ε, and ζ dihedrals for the model compounds As-T3PS or P-T3PS. Surfaces were obtained via MP2/6-31+G* optimizations with the remaining phospho- or arseno- diester dihedrals and selected furanose dihedrals constrained to values mimicking the A, B_I, and B_{II} of DNA (details in Table S1, supporting information). [Triangle, solid line: Phosphorus-T3PS, Circle, dashed line: Arsenic-T3PS]. Lower-panel: NDB survey data for the different forms of DNA (Black: A DNA, Red: B_I DNA, Green: B_{II} DNA).

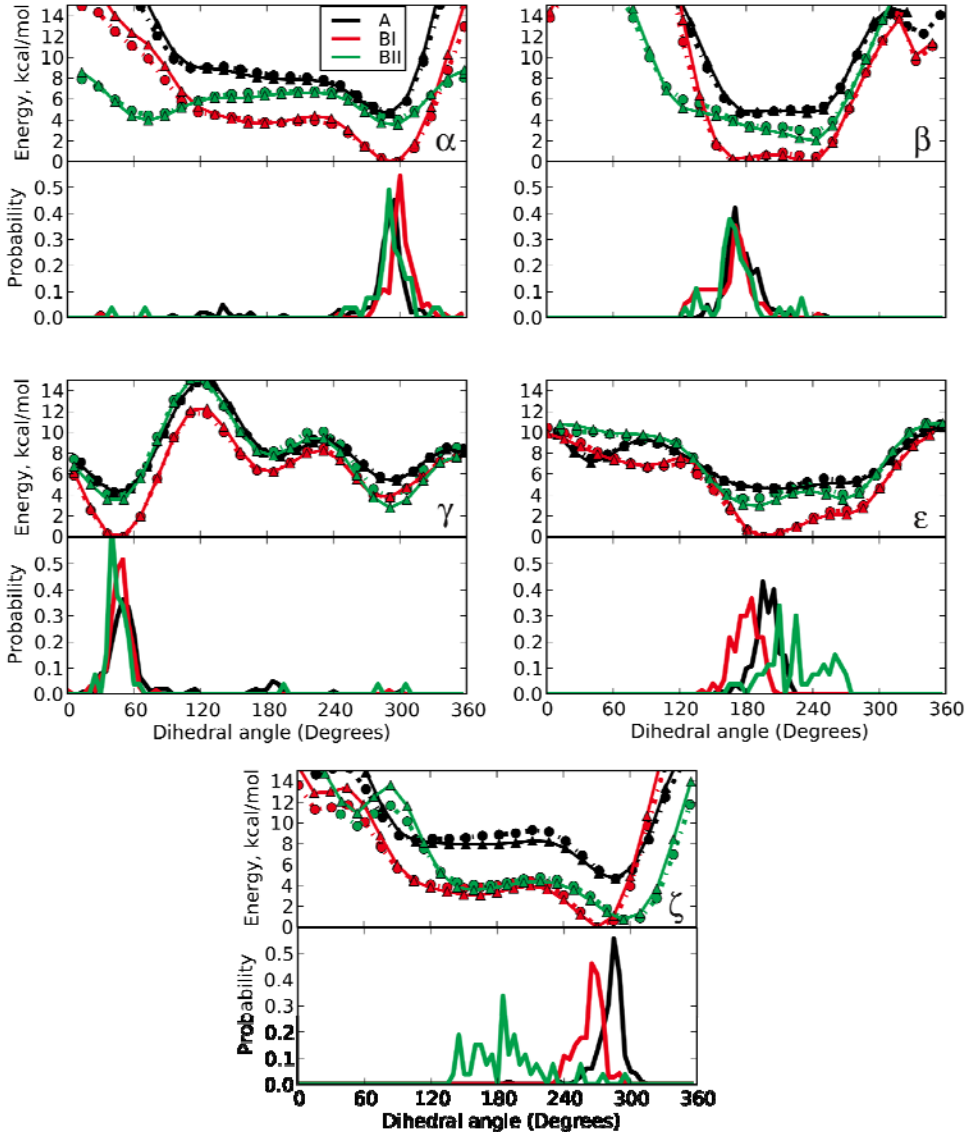

Figure S2. The C1' – C1' distance between the two sugars as a function of the α, β, γ, ε, and ζ torsion angles for the model compounds and the conformations representing the A, B_I, and B_{II} of DNA. [Triangle, solid line: P-T3PS, Circle, dashed line: As-T3PS]

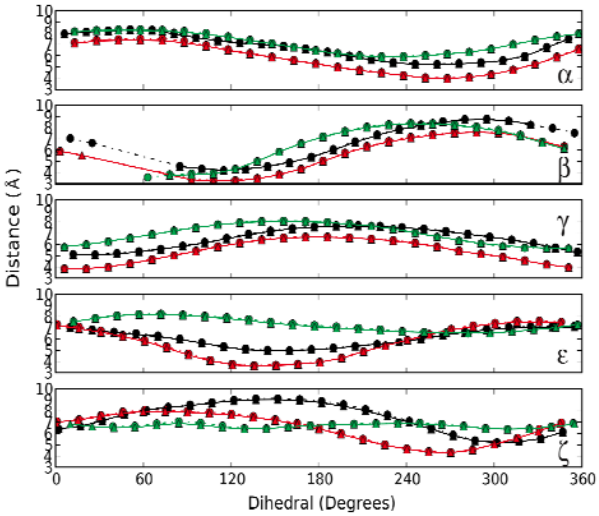

Table S1. Value of dihedral constraints used to mimic the A, B_I, and B_{II} forms of DNA.

Target Dihedral	A DNA	B_I DNA	B_{II} DNA
α (O32-P-O52-C52)	291	298	298
β (P-O52-C52-C42)	175	168	168
γ (O52-C52-C42-C32)	57	51	51
ε (C42-C32-O32-P)	205	195.7	267.2
ζ (C32-O32-P-O52)	287	270.3	159.2
Sugar constraints:			
C22 endo (south, B form)	C32-C42-O42-C12 = 0		
C32 endo (north, A form)	C42-O42-C12-C22 = 0		

Table S2. Relative energies at the RIMP2/cc-pVTZ level.of selected MP2/6-31+G(d) optimized low energy conformations

Target Dihedral	DNA form	Dihedral Angle	As-T3PS	P-T3PS
α	A	288	4.66	4.62
	B_I	293	0.0	0.0
	B_{II}	292	4.05	3.55
β	A	217	4.60	4.68
	B_I	193	0.0	0.0
	B_{II}	269	2.82	2.02
γ	A	286	4.29	4.28
	B_I	274	0.0	0.0
	B_{II}	273	3.67	2.77
ε	A	217	4.66	4.59
	B_I	193	0.0	0.0
	B_{II}	269	3.62	2.95
ζ	A	286	4.66	4.62
	B_I	273	0.0	0.0
	B_{II}	158	0.74	0.73

Energies in kcal/mol and dihedral angles in degrees.

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