Supporting Information

Table SI1. The main geometric parameters of the optimized structures of dGpdG$^-$, dGAsdG$^-$, and mono-hydrated dGAsdG$^-$. Angle in degree (°) and distance in Å.

	dGpdG$^-$	dGAsdG$^-$	dGAsdG$^-$
$\varphi(\boldsymbol{\tau}_1, \boldsymbol{\tau}_2)$[a]	8.8	9.1	9.5
$R(O_1, O_2)$	3.208	3.19	3.209
X—O3′	1.588 (1.58)[c]	1.736 (1.73)[d]	1.774
X—O5′	1.582 (1.58)[c]	1.730 (1.73)[d]	1.788
X—OH	1.597	1.745	1.646[b]
X═O	1.469 (1.47)[c]	1.621	1.652[b]

[a] $\boldsymbol{\tau}_1$: vector of base G1, defined by the N1, N3, and C5 atoms of G; $\boldsymbol{\tau}_2$: vector of base G2, defined by the N1, N3, and C5 atoms of G2. $\varphi(\boldsymbol{\tau}_1, \boldsymbol{\tau}_2)$: angle between $\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$. (see Figure 1). O_1: center of base G1, defined as the geometric center of the N1, N3, and C5 atoms of G1; O_2: center of base G2, defined as the geometric center of the N1, N3, and C5 atoms of G2. $R(O_1, O_2)$: distance between O_1 and O_2. X = P for dGpdG; X = As for dGAsdG$^-$.

[b] As—O bond lengths in mono-hydrated dGAsdG$^-$.

[c] Experiment, 7BNA, Ref. 2.

[d] Experiment, GFAJ1, Refs. 1, 2.

Table SI2. The relative energies along the reaction pathways of hydrolysis of $Me_2AsO_4^-$ and $Me_2PO_4^-$ (in Kcal/mol).[a]

.	ΔE	ΔE(PCM)	ΔE	ΔE(PCM)
Me_2AsO_4			$Me_2PO_4^-$	
R	0.00, **0.00**	**0.00**	0.00, **0.00**	**0.00**
TS01	19.83, **21.61**	**21.32**	35.49, **37.23**	**37.26**
Im1	6.97, **9.62**	**8.06**	30.54, **32.79**	**31.45**
TS12	15.89, **18.12**	**14.99**	41.52, **43.44**	**40.68**
Im2	6.66, **9.32**	**7.85**	30.17, **32.59**	**31.35**
TS23	22.64, **24.36**	**23.32**	34.64, **36.49**	**38.01**
P	2.01, **1.47**	**1.60**	2.72, **2.24**	**2.30**

[a] ΔE(PCM): relative energy in aqueous solution. Values in plain are calculated at the M06-2X/6-31+G(d,p) level of theory, in **bold** are with the M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) approach.

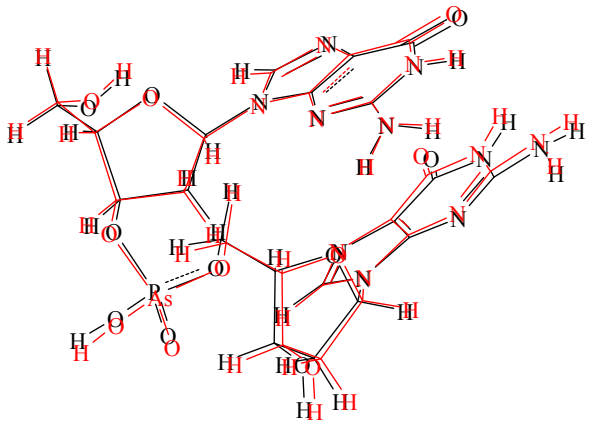

Figure SI. The superimposition of the optimized structures of dGpdG (black) and dGAsdG (red).