

Supplementary Information to the paper

Theoretical modeling on the kinetics of the arsenate-ester hydrolysis: implications to the stability of As-DNA

*Arnošt Mládek,^a Jiří Šponer,^a Bobby G. Sumpter,^b
Miguel Fuentes-Cabrera,^{b*} and Judit E. Šponer^{a*}*

^a Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135,
CZ-61265, Brno, Czech Republic

^b Center for Nanophase Materials Sciences, and Computer Sciences and Mathematics Division,
Oak Ridge National Laboratory, Oak Ridge, P. O. Box 2008, Oak Ridge, TN 37831-6494, USA

*corresponding authors: judit@ncbr.chemi.muni.cz, fuentesabma@ornl.gov

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Analysis of the variation of the reaction free energies

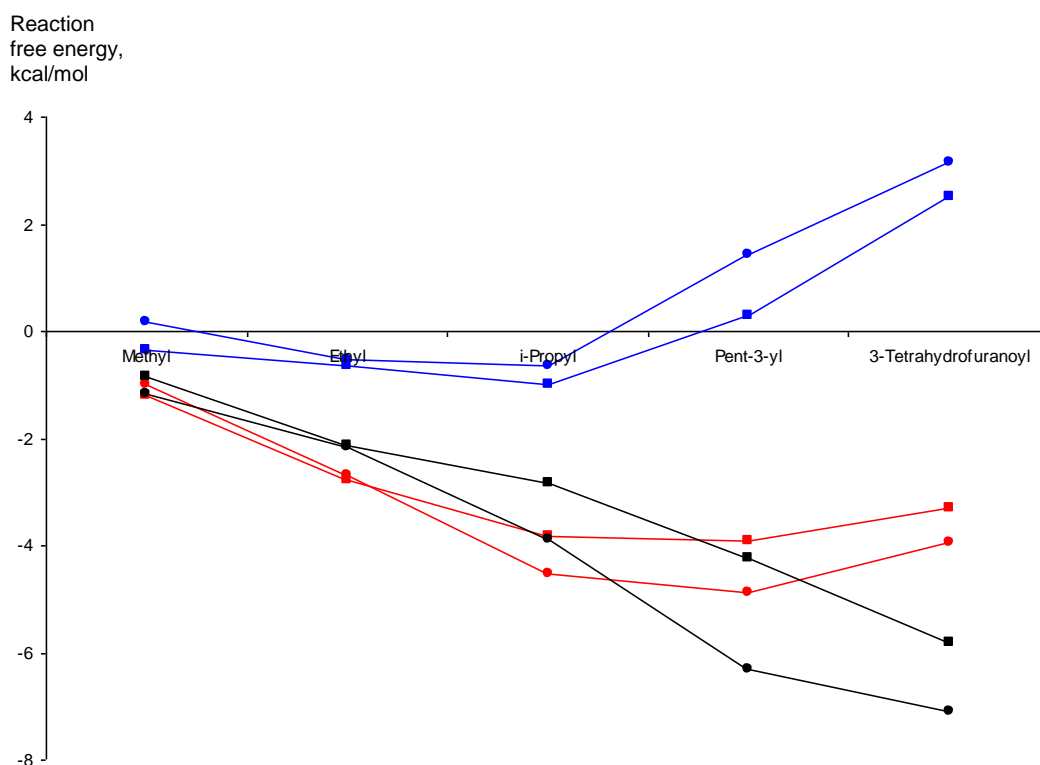
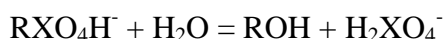


Figure S1. Reaction free energies computed at PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level for the hydrolysis of the studied phosphate- and arsenate-esters. The C-PCM dielectric continuum model was used to account for the effect of aqueous medium. ■: arsenates, ●: phosphates; blue: reaction free energies in gas-phase, red: reaction free energies in solution, black: solvent contribution to the reaction free energies.

We have computed the free energy change for the total hydrolysis reaction according to the following equation:



where X=As, P and R=methyl, ethyl, i-propyl, pent-3-yl, 3-tetrahydrofuranoyl.

There are two counteracting effects shaping the reaction free energies in solution (red curves). In gas-phase (blue curves) the hydrolysis products (i.e. alcohols and H_2XO_4^-) are destabilized as compared to the corresponding esters, most likely because the ester form gains an extra stabilization from the hyperconjugation between the phosphate-/arsenate-moiety and the alkyl group. With the increasing size of the alkyl group this effect becomes more pronounced, due to the extension of the electron delocalization along the alkyl chain, and this leads to the enhancement of the endothermic character of the gas-phase reaction. In contrast, the solvent contribution (black curves) seems to stabilize more the alcohols as compared to the esters, which shifts the reaction free energy changes into the exothermic direction. The steady increase of this exothermic contribution with the size of the alkyl group could be explained by steric effects. The major part of the solvation free energy is carried by the charged monoester anions. The larger is the alkyl group the worse is the ester solvated. Thus, with increasing size of the alkyl group, this leads to an increase of the solvent-related stabilization of the products of the hydrolysis reaction as compared to the reactants.

Optimized geometries of the computed models obtained at B3LYP/6-311++G(2d,2p) level

Abbreviations:

Im1: initial state complex, Ts1: transition state of the addition step, Im2: trigonal bipyramidal intermediate, Ts2: transition state of the dissociation step, Im3: primary product of the reaction, see Figure 1 in the paper.

Models used for the hydrolysis of **methyl-arsenate** monoanion:

Im1

As	0.119294	-0.328571	0.036538
O	-0.560367	0.252920	1.423982
O	1.716762	0.489648	-0.204702
O	-0.722452	-0.373278	-1.391446
O	0.795330	-1.976206	0.288695
C	1.686128	1.909011	-0.133555
H	0.573499	-2.447857	-0.522063
H	-2.452121	0.765183	0.696225
H	2.720564	2.254081	-0.183771
O	-3.071957	0.828487	-0.049897
H	-2.524210	0.447457	-0.757308
H	1.238334	2.254027	0.801504
H	1.131950	2.343334	-0.972085

Ts1

As	-0.130533	0.049446	0.088023
O	-0.481004	-0.930640	-1.295066
O	1.608732	0.501097	-0.322333
O	-0.065301	-0.558445	1.615644
O	-0.594587	1.762825	-0.134892
C	2.584546	-0.498201	-0.095696
H	0.248289	2.204044	-0.299445
H	-1.586399	-0.905025	-0.955521
H	3.566401	-0.045335	-0.256081
H	2.469793	-1.335163	-0.793103
H	2.532065	-0.883527	0.926244
O	-2.425343	-0.374481	-0.115434
H	-2.524939	-0.960806	0.640160

Im2

As	-0.296937	0.041596	0.155837
O	-0.308519	-0.926149	-1.375860
O	1.484342	0.538732	-0.292495
O	-0.002147	-0.643131	1.641352
O	-0.632869	1.786395	-0.126554
C	2.497330	-0.405243	-0.046577
H	0.246933	2.147855	-0.294314
H	-1.220561	-1.241153	-1.406327
H	3.466352	0.098168	-0.143094

H	2.469851	-1.229743	-0.771651
H	2.415893	-0.827721	0.959159
O	-2.167765	-0.227401	0.193636
H	-2.272402	-0.617905	1.067589

Ts2

As	0.444053	0.090947	0.011943
O	0.697013	-1.059317	-1.341417
O	-1.811774	-0.655821	-0.162046
O	0.108736	1.657245	-0.363102
O	-0.096648	-0.744378	1.422719
C	-2.793123	0.334273	-0.096276
H	-1.113916	-0.861574	0.934400
H	1.657503	-1.142978	-1.380318
H	-3.799082	-0.112844	-0.026657
H	-2.776061	0.973347	-0.988645
H	-2.671108	1.004890	0.768693
O	2.238335	0.153517	0.397911
H	2.450397	1.088165	0.302456

Im3

As	-0.758556	-0.419338	-0.273288
O	-0.129081	0.933087	0.755929
O	3.059328	-0.204836	-1.266317
O	-2.034570	0.204325	-1.119671
O	0.552301	-1.208700	-0.884542
C	3.463023	0.169360	0.032438
H	2.145184	-0.564961	-1.195246
H	-0.754706	1.651690	0.611323
H	2.710474	0.784608	0.535081
H	4.386449	0.748026	-0.053523
H	3.667655	-0.700832	0.671149
O	-1.470811	-1.507982	0.983056
H	-2.416553	-1.327533	0.942188

Models used for the hydrolysis of **methyl-phosphate** monoanion:

Im1:

P	-0.188299	0.413893	0.048986
O	0.485204	0.030203	1.325768
O	-1.628135	-0.393639	-0.064410
O	0.532744	0.323383	-1.266350
O	-0.812034	1.925684	0.186272
C	-1.541372	-1.809730	-0.088595
H	-0.784835	2.310802	-0.694198
H	2.388704	-0.536877	0.721599
H	-2.561200	-2.195921	-0.120149
O	2.987873	-0.672555	-0.031274
H	2.397783	-0.377595	-0.745214
H	-1.039440	-2.187432	0.805572
H	-1.000251	-2.158351	-0.973104

Ts1:

P	-0.159883	0.076785	0.099926
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O	-0.377455	-0.845168	-1.183423
O	1.437795	0.527429	-0.258104
O	-0.102214	-0.495836	1.471704
O	-0.670064	1.609866	-0.112697
C	2.442159	-0.441545	-0.036020
H	0.127449	2.130955	-0.259460
H	-1.408139	-0.957887	-0.987287
H	3.408160	0.039092	-0.206287
H	2.340509	-1.282551	-0.729439
H	2.399839	-0.821748	0.987366
O	-2.370651	-0.363665	-0.055279
H	-2.457364	-0.897420	0.738537

Im2:

P	-0.281301	0.049579	0.125250
O	-0.253924	-0.825983	-1.286499
O	1.399776	0.529228	-0.265348
O	-0.001903	-0.573510	1.470545
O	-0.624021	1.646603	-0.102669
C	2.417864	-0.406536	-0.039113
H	0.234479	2.061082	-0.249184
H	-1.145092	-1.188862	-1.345082
H	3.382223	0.086887	-0.207166
H	2.349155	-1.259272	-0.728549
H	2.385531	-0.791764	0.984631
O	-2.035103	-0.231020	0.162794
H	-2.148185	-0.602133	1.041088

Ts2:

P	0.533209	0.091477	0.017904
O	0.645714	-0.944697	-1.240981
O	-1.617499	-0.639369	-0.050017
O	0.143902	1.505377	-0.232299
O	0.240333	-0.679825	1.381012
C	-2.609723	0.325584	-0.105111
H	-0.752813	-0.865212	1.171274
H	1.588749	-1.017699	-1.422957
H	-3.611631	-0.126407	0.018645
H	-2.616765	0.859204	-1.070091
H	-2.511455	1.107218	0.669068
O	2.212058	0.191099	0.233562
H	2.397243	1.133163	0.197673

Im3:

P	1.007684	-0.059408	-0.124657
O	1.926606	-0.869176	-1.237400
O	-2.683882	-0.970040	0.036673
O	0.664808	1.271725	-0.723172
O	0.010953	-1.030826	0.412490
C	-2.971456	0.411481	0.087367
H	-1.712489	-1.064853	0.167722
H	2.129487	-0.231325	-1.927099
H	-3.040468	0.781604	1.120390
H	-3.939611	0.578923	-0.393225
H	-2.212931	1.005020	-0.430352

O	2.102124	0.211400	1.085550
H	2.400978	1.118275	0.976212

Models used for the hydrolysis of **ethyl-arsenate** monoanion:

Im1:

As	0.115091	-0.347125	0.012510
O	-0.552187	0.217924	1.412670
O	1.708404	0.478065	-0.233072
O	-0.739257	-0.377751	-1.408377
O	0.796410	-1.996150	0.240238
C	1.689555	1.900094	-0.135233
H	0.565270	-2.460988	-0.571860
H	-2.441859	0.780129	0.686101
C	3.125829	2.396394	-0.152775
O	-3.051736	0.867574	-0.065370
H	-2.506471	0.479223	-0.771214
H	1.188444	2.206321	0.786971
H	1.133654	2.329227	-0.976725
H	3.153691	3.487195	-0.091031
H	3.627467	2.089128	-1.071464
H	3.681095	1.986441	0.691632

Ts1

As	-0.491828	0.044408	0.099817
O	-0.801187	-0.902963	-1.315232
O	1.275488	0.458797	-0.224347
O	-0.509413	-0.588854	1.618343
O	-0.904310	1.772196	-0.112630
C	2.224040	-0.568937	0.009619
H	-0.045528	2.195298	-0.237479
H	-1.921028	-0.856313	-1.024488
C	3.621502	0.016348	-0.127253
H	2.085825	-1.379861	-0.715345
H	2.082437	-0.989406	1.009913
O	-2.781887	-0.320228	-0.212751
H	-2.929140	-0.917101	0.526626
H	4.379056	-0.753999	0.039297
H	3.774402	0.814167	0.601228
H	3.767582	0.433820	-1.124836

Im2:

As	-0.592157	0.032437	0.135457
O	-0.613205	-0.907167	-1.413149
O	1.228097	0.436908	-0.258707
O	-0.371073	-0.690607	1.615271
O	-0.823901	1.796433	-0.126649
C	2.187935	-0.566138	-0.025842
H	0.077316	2.111860	-0.271573
H	-1.538960	-1.173683	-1.474871
C	3.581187	0.047948	-0.106417
H	2.097203	-1.365480	-0.774894
H	2.029722	-1.018984	0.958005

O	-2.473791	-0.134559	0.122937
H	-2.620716	-0.539644	0.984103
H	4.351090	-0.711173	0.061192
H	3.696455	0.828993	0.647443
H	3.748300	0.497356	-1.087502

Ts2:

As	0.598201	0.139183	-0.018166
O	0.820748	-1.077374	-1.315652
O	-1.678095	-0.655882	-0.080191
O	0.223421	1.675697	-0.465624
O	0.101967	-0.629260	1.445278
C	-2.680662	0.311445	-0.035066
H	-0.920244	-0.787064	1.005214
H	1.780016	-1.160419	-1.378645
C	-4.068457	-0.330212	0.069376
H	-2.644189	0.939635	-0.936337
H	-2.546459	1.003211	0.813626
O	2.397593	0.240638	0.317315
H	2.599276	1.170565	0.168141
H	-4.858310	0.429102	0.086945
H	-4.145265	-0.928890	0.980008
H	-4.241742	-0.992976	-0.781020

Im3:

As	0.816507	0.019308	-0.074454
O	2.047356	0.615754	-1.255707
O	-2.697537	-1.740596	-0.398567
O	0.213685	1.355506	0.694037
O	-0.062345	-1.137090	-0.852387
C	-3.393789	-0.537991	-0.659118
H	-1.734827	-1.562753	-0.505074
H	2.170147	1.542775	-1.022750
C	-3.366044	0.439080	0.514830
H	-4.428435	-0.816900	-0.885142
H	-2.988740	-0.046340	-1.552032
O	1.876334	-0.816323	1.129369
H	1.892107	-0.216475	1.883551
H	-3.970910	1.324332	0.291747
H	-2.346944	0.766677	0.724028
H	-3.771066	-0.037562	1.410071

Models used for the hydrolysis of **ethyl-phosphate** monoanion:

Im1:

P	0.157519	-0.306359	0.050884
O	-0.508418	0.126034	1.315795
O	1.637524	0.427316	-0.057447
O	-0.543909	-0.195762	-1.273481
O	0.702379	-1.845910	0.213228
C	1.632138	1.849110	-0.106300
H	0.652344	-2.244958	-0.659987
H	-2.407827	0.713275	0.690459
C	3.070124	2.333503	-0.180668

O	-2.997942	0.845081	-0.069995
H	-2.404104	0.535439	-0.774581
H	1.136231	2.245175	0.784454
H	1.068641	2.187936	-0.981701
H	3.104328	3.425066	-0.217967
H	3.562181	1.941664	-1.072116
H	3.632192	1.999090	0.692422

Ts1:

P	-0.586781	0.065179	0.110883
O	-0.794224	-0.814470	-1.203089
O	1.041373	0.457455	-0.178345
O	-0.602176	-0.541678	1.468945
O	-1.026412	1.622780	-0.079359
C	2.007469	-0.553234	0.046659
H	-0.204398	2.114112	-0.188287
H	-1.836139	-0.888869	-1.045553
C	3.394220	0.055174	-0.092869
H	1.874788	-1.361768	-0.680960
H	1.868943	-0.977350	1.044737
O	-2.805362	-0.280121	-0.134407
H	-2.942727	-0.830295	0.640832
H	4.164182	-0.703491	0.068910
H	3.537621	0.852640	0.638171
H	3.532222	0.478812	-1.089137

Im2:

P	-0.708104	0.038700	0.132907
O	-0.652364	-0.786742	-1.307420
O	1.015999	0.449571	-0.165433
O	-0.517974	-0.641884	1.465365
O	-0.962065	1.656865	-0.051831
C	1.986730	-0.534532	0.067617
H	-0.079347	2.034117	-0.144437
H	-1.555504	-1.103731	-1.422310
C	3.372801	0.076115	-0.110522
H	1.863456	-1.371106	-0.635016
H	1.876055	-0.942006	1.077941
O	-2.470411	-0.158072	0.081043
H	-2.642593	-0.554742	0.938380
H	4.153414	-0.671279	0.060942
H	3.521361	0.896727	0.594611
H	3.492645	0.474199	-1.120439

Ts2:

P	0.545389	0.096059	0.019039
O	0.630630	-0.948406	-1.233343
O	-1.614644	-0.631785	-0.009989
O	0.150239	1.507637	-0.229994
O	0.277633	-0.666727	1.393419
C	-2.611873	0.323183	-0.086361
H	-0.713231	-0.854924	1.220027
H	1.569283	-1.023817	-1.436101
C	-4.004074	-0.312970	0.029867
H	-2.559679	0.873918	-1.041199

H	-2.518260	1.098163	0.697147
O	2.225766	0.192742	0.204540
H	2.414173	1.134130	0.167464
H	-4.797231	0.440688	-0.044128
H	-4.107380	-0.829751	0.987594
H	-4.148940	-1.050740	-0.762780

Im3:

P	0.788854	-0.006730	-0.053477
O	1.870159	0.517033	-1.188577
O	-2.651973	-1.719655	-0.463236
O	0.192679	1.207586	0.593974
O	-0.002622	-1.097724	-0.692031
C	-3.336696	-0.502765	-0.680467
H	-1.685187	-1.533166	-0.498471
H	2.017843	1.449506	-1.008384
C	-3.318464	0.422557	0.534837
H	-4.369350	-0.765381	-0.934166
H	-2.915781	0.026674	-1.544532
O	1.784098	-0.711636	1.064224
H	1.832319	-0.097227	1.801645
H	-3.911618	1.322783	0.341091
H	-2.297618	0.727767	0.767049
H	-3.741144	-0.088221	1.402924

Models used for the hydrolysis of **i-propyl-arsenate** monoanion:

Im1:

As	0.027850	0.680799	-0.363425
O	-0.718455	-0.376637	-1.388113
O	1.818283	0.588757	-0.612544
O	-0.303707	0.688458	1.261520
O	-0.153345	2.369288	-0.952982
C	2.429790	-0.687392	-0.379126
H	-0.249274	2.894796	-0.150774
H	-1.937942	-1.398630	-0.001268
C	3.813752	-0.418708	0.202278
C	2.481172	-1.493380	-1.674819
H	1.847403	-1.244124	0.362770
O	-2.210929	-1.529149	0.921891
H	-1.685282	-0.833404	1.353496
H	4.339391	-1.354895	0.404721
H	3.729365	0.144118	1.131335
H	4.408116	0.167208	-0.501837
H	2.932759	-2.474514	-1.504279
H	3.075300	-0.961635	-2.421467
H	1.472651	-1.626457	-2.062577

Ts1:

As	-0.177730	0.047551	0.044565
O	-0.804888	-0.976117	-1.201831
O	1.520605	0.322408	-0.624150
O	0.062695	-0.472747	1.587784
O	-0.538864	1.775529	-0.241616

C	2.545858	-0.600661	-0.265179
H	0.310522	2.132451	-0.530709
H	-1.843640	-0.830646	-0.712221
C	3.850992	0.182149	-0.148872
C	2.635025	-1.722769	-1.299953
H	2.304876	-1.029317	0.711881
O	-2.500192	-0.180010	0.200994
H	-2.538542	-0.712728	1.000573
H	4.678754	-0.475873	0.127257
H	3.757239	0.959136	0.609924
H	4.093050	0.659380	-1.101388
H	3.395636	-2.456012	-1.016984
H	2.892824	-1.313524	-2.279557
H	1.673577	-2.226496	-1.388818

Im2:

As	-0.271398	0.062598	0.128039
O	-0.644212	-1.067882	-1.236232
O	1.463354	0.274759	-0.644942
O	0.193429	-0.476868	1.630191
O	-0.462317	1.784742	-0.348876
C	2.496443	-0.627736	-0.301651
H	0.413543	2.005553	-0.691728
H	-1.581127	-1.252997	-1.092174
C	3.780127	0.173941	-0.077505
C	2.672433	-1.682574	-1.398847
H	2.234366	-1.124911	0.636833
O	-2.124689	0.044030	0.490032
H	-2.124955	-0.227692	1.413759
H	4.615748	-0.479727	0.188951
H	3.632291	0.894464	0.727133
H	4.047531	0.722239	-0.984826
H	3.449626	-2.405867	-1.132318
H	2.952607	-1.204542	-2.341353
H	1.734105	-2.212131	-1.555888

Ts2:

As	0.519806	0.061638	0.095593
O	0.856547	-0.837567	-1.416320
O	-1.766633	-0.558884	-0.407159
O	0.253675	1.679966	-0.018532
O	-0.182424	-0.985540	1.273501
C	-2.758962	0.414124	-0.264057
H	-1.146057	-0.976608	0.705894
H	1.811887	-0.970696	-1.388780
C	-4.098371	-0.248110	0.094979
C	-2.877381	1.240792	-1.549048
H	-2.504444	1.115050	0.548681
O	2.262839	-0.028034	0.648992
H	2.514798	0.896670	0.744552
H	-3.648884	2.013199	-1.462490
H	-3.129210	0.586919	-2.388356
H	-1.922564	1.721909	-1.755064
H	-4.892420	0.493158	0.232951
H	-3.999302	-0.822393	1.017993

H -4.397500 -0.936791 -0.699229

Im3:

As 1.195950 -0.167036 0.259860
O 2.678630 0.575159 -0.458849
O -2.410004 -0.982989 -1.194179
O 0.666427 0.876144 1.430780
O 0.303907 -0.752814 -0.995439
C -2.914255 0.338624 -1.102508
H -1.432914 -0.949197 -1.069124
H 2.885370 1.309361 0.130147
C -2.894434 0.851224 0.339382
C -4.323606 0.326604 -1.686850
H -2.291542 1.007397 -1.711930
O 1.909691 -1.582642 1.129109
H 1.894960 -1.321044 2.056552
H -3.286254 1.871403 0.397306
H -1.879281 0.854472 0.736963
H -3.512253 0.207243 0.970521
H -4.770303 1.323007 -1.661281
H -4.959080 -0.351838 -1.112945
H -4.303607 -0.022279 -2.720014

Models used for the hydrolysis of **i-propyl-phosphate** monoanion:

Im1:

P 0.083048 0.693788 -0.385781
O -0.630535 -0.248337 -1.300404
O 1.712267 0.587789 -0.651105
O -0.174380 0.672586 1.094910
O -0.115021 2.231457 -0.921461
C 2.333711 -0.676098 -0.387342
H -0.080518 2.798511 -0.145855
H -1.796759 -1.396583 -0.004734
C 3.696561 -0.392294 0.233997
C 2.428804 -1.485898 -1.677460
H 1.728831 -1.228713 0.337293
O -2.026824 -1.566496 0.923539
H -1.504826 -0.858383 1.338153
H 4.224318 -1.322955 0.455399
H 3.577905 0.171623 1.158730
H 4.307636 0.197266 -0.452922
H 2.874957 -2.466108 -1.488750
H 3.045670 -0.957595 -2.408229
H 1.432055 -1.619059 -2.093177

Ts1:

P -0.206388 0.135661 -0.087601
O -1.329971 1.261106 -0.217486
O 1.121341 1.191461 0.031728
O 0.123730 -0.770712 -1.220844
O 0.020177 -0.367314 1.445361
C 1.694150 1.730831 -1.155635
H 0.836591 0.054199 1.736944

H	-2.112191	0.558451	-0.124046
C	3.210816	1.729824	-0.984187
C	1.143290	3.132476	-1.417788
H	1.435397	1.074725	-1.989926
O	-2.206554	-0.866344	0.203036
H	-2.207189	-1.405003	-0.592171
H	3.704840	2.139406	-1.868785
H	3.569379	0.713008	-0.824908
H	3.495725	2.335131	-0.120138
H	1.554753	3.545188	-2.343277
H	1.403486	3.802007	-0.594296
H	0.058418	3.095597	-1.495480

Im2:

P	0.914410	-0.244764	0.053351
O	1.000045	1.414946	0.072684
O	-0.718526	-0.037539	-0.672114
O	0.490099	-1.038910	1.264458
O	1.303670	-0.906920	-1.404033
C	-1.796995	0.315955	0.163761
H	0.470835	-0.935409	-1.890001
H	1.884905	1.592086	0.412378
C	-2.661403	-0.912066	0.461345
C	-2.595240	1.431932	-0.514706
H	-1.413695	0.693219	1.116143
O	2.645657	-0.257644	0.427260
H	2.668603	-0.814415	1.209244
H	-3.501148	-0.661584	1.117942
H	-2.041863	-1.665603	0.943675
H	-3.062469	-1.323906	-0.469302
H	-3.440608	1.750776	0.102850
H	-2.983653	1.087513	-1.476906
H	-1.947525	2.289436	-0.696329

Ts2:

P	0.564171	0.074806	0.100306
O	0.742300	-0.690493	-1.330256
O	-1.592715	-0.578299	-0.241199
O	0.198489	1.516469	0.119502
O	0.186950	-0.948378	1.264308
C	-2.596196	0.377562	-0.249387
H	-0.788455	-1.073027	0.997494
H	1.693716	-0.754327	-1.467655
C	-3.924049	-0.241017	0.221906
C	-2.752728	0.991533	-1.650749
H	-2.355418	1.209813	0.434819
O	2.223173	0.095279	0.432103
H	2.420005	1.020687	0.599210
H	-3.531284	1.762835	-1.675382
H	-3.009155	0.209885	-2.371677
H	-1.806925	1.440322	-1.950798
H	-4.735542	0.495031	0.237984
H	-3.809737	-0.650430	1.227816
H	-4.209801	-1.060654	-0.443248

Im3:

P	1.163211	-0.157023	0.253184
O	2.519870	0.469277	-0.451869
O	-2.352880	-0.965241	-1.230042
O	0.680971	0.836619	1.267446
O	0.326930	-0.706326	-0.853152
C	-2.874825	0.345058	-1.096617
H	-1.382591	-0.927206	-1.058495
H	2.799244	1.201106	0.105038
C	-2.856848	0.814188	0.359890
C	-4.284976	0.331419	-1.679044
H	-2.263167	1.042152	-1.685879
O	1.778147	-1.443860	1.090788
H	1.786672	-1.179538	2.014734
H	-3.261278	1.827370	0.449205
H	-1.838746	0.817029	0.749422
H	-3.464773	0.143706	0.973066
H	-4.743790	1.321269	-1.625828
H	-4.910989	-0.370258	-1.122848
H	-4.262781	0.011059	-2.721500

Models used for the hydrolysis of **pent-3-yl-arsenate** monoanion:

Im1:

As	-0.095133	0.733908	-0.360272
O	-0.961767	0.078759	-1.599643
O	1.669027	0.725160	-0.778652
O	-0.253997	0.209500	1.205732
O	-0.304395	2.519530	-0.384307
C	2.438813	-0.411549	-0.370851
H	-0.146451	2.804302	0.522671
H	-1.917517	-1.478728	-0.538644
C	3.889055	0.062903	-0.193468
C	2.231173	-1.622085	-1.307549
H	2.099883	-0.720557	0.622746
O	-2.046956	-1.952419	0.299646
H	-1.528002	-1.388092	0.898100
H	4.476861	-0.781604	0.180426
H	3.873939	0.808477	0.605137
C	4.575348	0.673064	-1.418894
H	3.023772	-2.349328	-1.099349
C	2.151015	-1.327657	-2.808511
H	1.295070	-2.102032	-1.014664
H	5.527743	1.127786	-1.136222
H	3.948521	1.446008	-1.861592
H	4.785006	-0.072662	-2.185574
H	1.949476	-2.250698	-3.356987
H	3.070891	-0.900093	-3.206257
H	1.334924	-0.635993	-3.008123

Ts1:

As	-0.187102	0.066772	0.033322
O	-0.867520	-0.862008	-1.257988
O	1.491424	0.353277	-0.681331

O	0.098322	-0.550099	1.532500
O	-0.530151	1.814558	-0.131940
C	2.537093	-0.556168	-0.350861
H	0.315912	2.178495	-0.421439
H	-1.889947	-0.734428	-0.723857
C	3.846723	0.241360	-0.237840
C	2.558777	-1.765408	-1.312131
H	2.342878	-0.955098	0.649094
O	-2.498915	-0.138141	0.252225
H	-2.522031	-0.723076	1.015056
H	4.640091	-0.448067	0.069233
H	3.707629	0.940688	0.590240
C	4.294992	1.028889	-1.472812
H	3.491527	-2.317130	-1.148689
C	2.363449	-1.464289	-2.800938
H	1.749559	-2.429622	-1.002130
H	5.124464	1.694968	-1.223209
H	3.476878	1.637111	-1.857239
H	4.632539	0.374851	-2.276525
H	2.286695	-2.396530	-3.365619
H	3.183610	-0.887148	-3.227902
H	1.439402	-0.907858	-2.944320

Im2:

As	-0.426798	0.049194	0.125664
O	-0.684414	-0.995428	-1.329335
O	1.309195	0.428616	-0.588877
O	0.042231	-0.557808	1.599564
O	-0.726265	1.783906	-0.235079
C	2.412217	-0.370908	-0.213582
H	0.141809	2.088992	-0.529073
H	-1.610674	-1.251554	-1.233453
C	3.629460	0.544183	0.026899
C	2.636028	-1.535395	-1.207064
H	2.194670	-0.830306	0.755229
O	-2.280390	-0.124179	0.430669
H	-2.286786	-0.459163	1.333252
H	3.591618	-2.018266	-0.969860
C	2.564906	-1.190636	-2.697634
H	1.856991	-2.272368	-1.002758
H	4.476235	-0.077822	0.337851
H	3.371800	1.167802	0.886638
C	4.054079	1.459183	-1.126025
H	2.588280	-2.102179	-3.300819
H	3.391028	-0.559561	-3.026403
H	1.632272	-0.670335	-2.907475
H	4.783203	2.198750	-0.784550
H	3.191472	1.992986	-1.523919
H	4.512036	0.905495	-1.945763

Ts2:

As	0.531750	0.035107	0.124477
O	0.926049	-0.756819	-1.432118
O	-1.742707	-0.578706	-0.514653
O	0.248177	1.653459	0.108400

O	-0.211837	-1.092275	1.197658
C	-2.745998	0.379210	-0.365457
H	-1.150065	-1.053743	0.602049
H	1.882297	-0.879014	-1.388921
C	-4.095316	-0.291384	-0.005718
C	-2.788718	1.327335	-1.589216
H	-2.524168	1.041189	0.489192
O	2.249817	-0.083102	0.737521
H	2.489747	0.832313	0.916963
H	-3.677868	1.965992	-1.519336
C	-2.717567	0.656130	-2.964772
H	-1.921018	1.980979	-1.486013
H	-4.859365	0.486420	0.110815
H	-3.960675	-0.740768	0.982945
C	-4.592572	-1.379384	-0.962403
H	-2.558316	1.402694	-3.747810
H	-3.625859	0.106938	-3.216381
H	-1.884726	-0.045294	-2.985114
H	-5.418930	-1.942520	-0.519890
H	-3.783333	-2.074287	-1.185282
H	-4.948898	-0.965069	-1.905938

Im3:

As	1.541846	-0.347201	0.306853
O	1.758336	-1.135493	1.918226
O	-1.676171	-0.296111	-1.961760
O	3.054485	0.047229	-0.228724
O	0.400352	-1.233137	-0.488394
C	-2.500857	0.309987	-0.980124
H	-0.872986	-0.634923	-1.499226
H	2.683866	-0.980249	2.137320
C	-3.167966	-0.741061	-0.068848
C	-3.448979	1.295747	-1.686259
H	-1.873653	0.912664	-0.313318
O	0.750843	1.210304	0.786062
H	1.441402	1.873668	0.677284
H	-3.745549	-0.216389	0.700636
H	-2.350650	-1.246676	0.449027
C	-4.040849	-1.797360	-0.752622
H	-4.190071	1.649082	-0.962126
C	-4.145792	0.787093	-2.953375
H	-2.849601	2.167139	-1.962745
H	-4.671626	1.604578	-3.453174
H	-4.875109	0.005368	-2.745548
H	-3.410285	0.379444	-3.644969
H	-4.275949	-2.608114	-0.059302
H	-3.515874	-2.227057	-1.605483
H	-4.988267	-1.389028	-1.107711

Models used for the hydrolysis of **pent-3-yl-phosphate** monoanion:

Im1:

P	0.676631	-0.494093	-0.617460
O	1.074232	0.773527	-1.297831

O	-0.952865	-0.735322	-0.789663
O	1.043759	-0.760029	0.815214
O	1.179843	-1.751854	-1.543099
C	-1.839882	-0.110412	0.142707
H	1.234776	-2.522260	-0.970410
H	2.114158	1.813299	0.181362
C	-3.103519	-0.978954	0.224266
C	-2.060710	1.383422	-0.177921
H	-1.375612	-0.157147	1.131902
O	2.398802	1.817176	1.110115
H	2.075227	0.938764	1.371033
H	-3.762405	-0.545288	0.983262
H	-2.784870	-1.950813	0.609050
C	-3.881977	-1.199566	-1.075794
H	-2.918669	1.729906	0.409194
C	-2.231659	1.752538	-1.654359
H	-1.190203	1.923791	0.196814
H	-4.650703	-1.963440	-0.935891
H	-3.213888	-1.532316	-1.869254
H	-4.381830	-0.292052	-1.413822
H	-2.320697	2.836608	-1.758024
H	-3.116290	1.303675	-2.105412
H	-1.355551	1.432841	-2.214777

Ts1:

P	0.765157	-0.110546	-0.024384
O	0.904134	1.309778	-0.735458
O	-0.824498	-0.432255	-0.543383
O	0.719420	-0.248057	1.456655
O	1.344873	-1.331740	-0.934604
C	-1.926224	-0.004758	0.250631
H	0.568280	-1.782919	-1.284079
H	1.936953	1.370379	-0.515903
C	-3.025205	-1.075765	0.159991
C	-2.352622	1.437928	-0.097322
H	-1.600948	0.006996	1.293742
O	2.941685	0.467053	0.037381
H	3.030298	0.584381	0.986509
H	-3.852656	-0.769961	0.808521
H	-2.604901	-1.982142	0.602751
C	-3.560246	-1.416439	-1.234312
H	-3.306304	1.641355	0.403044
C	-2.438783	1.793355	-1.584414
H	-1.615295	2.101230	0.357430
H	-4.192779	-2.306687	-1.195889
H	-2.739295	-1.615253	-1.922545
H	-4.159456	-0.608454	-1.653292
H	-2.625572	2.863245	-1.704906
H	-3.235756	1.260741	-2.103403
H	-1.494161	1.560535	-2.071561

Im2:

P	-0.388079	0.071822	0.086151
O	-0.579138	-0.951518	-1.206413
O	1.266977	0.411850	-0.577971

O	0.047253	-0.408720	1.447201
O	-0.683525	1.646459	-0.293055
C	2.368581	-0.381714	-0.207881
H	0.170559	1.986891	-0.585245
H	-1.492541	-1.250780	-1.125729
C	3.584025	0.535068	0.040205
C	2.607410	-1.542819	-1.204178
H	2.148840	-0.845030	0.758088
O	-2.124578	-0.100174	0.377284
H	-2.143811	-0.363929	1.300214
H	3.567894	-2.016207	-0.966354
C	2.537581	-1.193192	-2.693708
H	1.835147	-2.287583	-1.004571
H	4.433077	-0.084996	0.349462
H	3.321593	1.153628	0.902233
C	4.008326	1.457829	-1.106888
H	2.561651	-2.101754	-3.301911
H	3.363576	-0.560138	-3.019573
H	1.605243	-0.670834	-2.899630
H	4.732629	2.200115	-0.760388
H	3.143917	1.988568	-1.505183
H	4.471592	0.910358	-1.928057

Ts2:

P	0.543497	0.041940	0.099082
O	0.765610	-0.644581	-1.365295
O	-1.597121	-0.605215	-0.344510
O	0.161671	1.476167	0.188811
O	0.144936	-1.048127	1.194088
C	-2.609050	0.340508	-0.335256
H	-0.819584	-1.167550	0.900857
H	1.720646	-0.691879	-1.483394
C	-3.943670	-0.288112	0.143636
C	-2.698952	1.090740	-1.693193
H	-2.394457	1.136980	0.398874
O	2.191212	0.056163	0.474906
H	2.376312	0.970881	0.703249
H	-3.600369	1.716964	-1.705596
C	-2.633638	0.215313	-2.948757
H	-1.844654	1.769908	-1.709610
H	-4.727384	0.479408	0.136502
H	-3.791239	-0.563921	1.191978
C	-4.419520	-1.532804	-0.612513
H	-2.491582	0.829491	-3.843008
H	-3.538152	-0.376087	-3.099209
H	-1.792254	-0.471012	-2.863008
H	-5.227138	-2.037318	-0.073996
H	-3.591117	-2.231689	-0.726813
H	-4.793505	-1.290769	-1.608027

Im3:

P	1.224613	-0.146357	0.500528
O	2.591162	-0.133037	-0.431596
O	-1.761271	-0.889538	-1.667499
O	0.786545	1.278657	0.654822

O	0.349272	-1.245568	-0.004264
C	-2.427825	0.225360	-1.094874
H	-0.968137	-1.072660	-1.109823
H	2.814436	0.792947	-0.559512
C	-3.290628	-0.194490	0.113761
C	-3.158683	0.986508	-2.216386
H	-1.680229	0.914985	-0.689205
O	1.812273	-0.655047	1.957441
H	1.967080	0.137108	2.479310
H	-3.757165	0.701580	0.538056
H	-2.589331	-0.560307	0.866354
C	-4.348641	-1.273822	-0.133729
H	-3.792371	1.756540	-1.764536
C	-3.973253	0.139764	-3.200695
H	-2.391187	1.516019	-2.786733
H	-4.309837	0.750605	-4.042455
H	-4.857235	-0.302347	-2.742611
H	-3.359507	-0.670909	-3.590410
H	-4.737878	-1.656319	0.812873
H	-3.912477	-2.109582	-0.680587
H	-5.198827	-0.900588	-0.706530

Models used for the hydrolysis of **3-tetrahydrofuranoyl-arsenate** monoanion:

Im1:

As	0.092662	0.446469	-0.011307
O	-0.845572	0.329752	-1.362495
O	1.640560	-0.470578	-0.273434
O	-0.484848	0.069515	1.495730
O	0.849346	2.072263	0.065077
H	0.960946	2.252578	1.005238
H	-2.677417	-0.229406	-0.455881
O	-3.163126	-0.472780	0.349089
H	-2.460724	-0.369725	1.013110
C	2.970296	-2.459423	-0.084274
O	3.331707	-2.997885	-1.368301
C	2.326303	-2.608399	-2.317375
C	1.040301	-2.510006	-1.509452
C	1.545470	-1.892528	-0.194353
H	3.034854	-3.269009	0.645970
H	2.307642	-3.365066	-3.101427
H	2.580464	-1.640427	-2.760507
H	0.636273	-3.507309	-1.320271
H	0.271065	-1.888190	-1.962532
H	3.659096	-1.661987	0.199144
H	0.931300	-2.174759	0.662651

Ts1:

As	-0.188743	0.048387	0.051209
O	-0.688597	-0.929719	-1.286663
O	1.546570	0.401064	-0.494277
O	-0.019883	-0.542436	1.578148
O	-0.575933	1.778647	-0.172754
H	0.277869	2.175444	-0.386678

H	-1.771453	-0.835241	-0.853262
O	-2.481902	-0.249002	0.042540
H	-2.560701	-0.824781	0.808771
C	3.925023	0.118860	-0.282310
O	4.511315	-0.311550	-1.525479
C	3.525333	-1.059658	-2.255105
C	2.632045	-1.680876	-1.191557
C	2.545844	-0.547484	-0.152933
H	4.600277	-0.177140	0.524157
H	4.057359	-1.782347	-2.874220
H	2.948108	-0.391978	-2.902295
H	3.118692	-2.555375	-0.752191
H	1.642403	-1.956284	-1.548937
H	3.813243	1.204243	-0.276916
H	2.365634	-0.922170	0.855552

Im2:

As	0.989553	-0.141857	0.091055
O	0.858216	1.468332	-0.726580
O	-0.806367	-0.471270	-0.505916
O	0.732219	-0.343533	1.719848
O	1.389882	-1.450865	-1.069720
H	0.520337	-1.740942	-1.374415
H	1.752229	1.819732	-0.626423
O	2.835151	0.204511	0.224115
H	2.975743	0.098299	1.170699
C	-3.098245	-0.970091	0.048948
O	-4.015453	-0.244170	-0.796282
C	-3.375685	0.972609	-1.210799
C	-2.415860	1.320441	-0.082725
C	-1.877209	-0.069812	0.315978
H	-3.630950	-1.227022	0.968084
H	-4.160537	1.710795	-1.381848
H	-2.828390	0.811386	-2.145589
H	-2.962055	1.770177	0.751196
H	-1.600879	1.975258	-0.380076
H	-2.777734	-1.885972	-0.449822
H	-1.570064	-0.107004	1.361970

Ts2:

As	0.560631	0.063241	0.064550
O	0.826555	-0.875671	-1.434627
O	-1.786741	-0.585795	-0.328052
O	0.266000	1.670840	-0.090489
O	-0.107087	-0.953239	1.287573
H	-1.084363	-0.965038	0.773133
H	1.779671	-1.025832	-1.446390
O	2.315172	-0.012269	0.560381
H	2.575492	0.912801	0.625759
C	-4.166284	-0.205379	-0.015182
O	-4.810705	-0.162878	-1.306674
C	-3.871411	0.355743	-2.263486
C	-2.923759	1.231142	-1.458677
C	-2.751498	0.401100	-0.168246
H	-4.789064	0.360891	0.685769

H	-4.444175	0.889715	-3.024105
H	-3.326713	-0.467183	-2.736640
H	-3.392268	2.195105	-1.239786
H	-1.959041	1.403037	-1.928152
H	-4.089486	-1.240498	0.321429
H	-2.528323	1.062365	0.681514

Im3:

As	1.187467	-0.331019	0.827660
O	2.094006	1.216883	1.032069
O	-2.659221	-0.852697	0.501398
O	2.262794	-1.548423	1.128272
O	-0.285103	-0.100131	1.534951
H	-1.790635	-0.652006	0.929547
H	3.015613	0.945726	1.109083
O	0.899681	-0.335279	-0.961656
H	1.520949	-0.987447	-1.304580
C	-2.987392	1.411668	-0.397730
O	-4.409268	1.642715	-0.540200
C	-5.054915	0.390644	-0.785288
C	-3.993881	-0.482661	-1.446520
C	-2.728411	-0.080365	-0.680277
H	-2.471235	2.058804	-1.110589
H	-5.926748	0.584043	-1.412675
H	-5.388570	-0.056010	0.157575
H	-3.897704	-0.223902	-2.503080
H	-4.183936	-1.550318	-1.353588
H	-2.667160	1.663690	0.612304
H	-1.820127	-0.209015	-1.272973

Models used for the hydrolysis of **3-tetrahydrofuranoyl-phosphate** monoanion:

Im1:

P	0.153234	0.431702	-0.027815
O	-0.714215	0.319232	-1.237617
O	1.555739	-0.425963	-0.270587
O	-0.368687	0.098646	1.340343
O	0.826300	1.924092	0.004257
H	1.049896	2.114197	0.920003
H	-2.558905	-0.322168	-0.453278
O	-3.028971	-0.599607	0.349410
H	-2.321352	-0.452001	0.999010
C	2.894435	-2.408906	-0.050544
O	3.282620	-2.950932	-1.326005
C	2.292553	-2.570538	-2.295327
C	0.992074	-2.467126	-1.511961
C	1.471084	-1.846993	-0.189281
H	2.947074	-3.216556	0.682688
H	2.289145	-3.333452	-3.073768
H	2.553776	-1.605901	-2.741841
H	0.581190	-3.462398	-1.327650
H	0.233751	-1.840456	-1.975033
H	3.576666	-1.609714	0.243468
H	0.839194	-2.122058	0.655929

Ts1:

P	-0.140237	0.055599	0.022694
O	-0.569283	-0.855989	-1.211501
O	1.457622	0.357874	-0.502011
O	0.016809	-0.499285	1.394243
O	-0.533998	1.622418	-0.177964
H	0.289243	2.073802	-0.395597
H	-1.588846	-0.862289	-0.899429
O	-2.371767	-0.187934	0.103805
H	-2.431488	-0.713477	0.905578
C	3.839509	0.127787	-0.258098
O	4.464153	-0.285308	-1.488975
C	3.508454	-1.043392	-2.247197
C	2.602165	-1.689273	-1.209566
C	2.473768	-0.570593	-0.159959
H	4.504122	-0.154553	0.561617
H	4.066971	-1.751132	-2.860334
H	2.934866	-0.379878	-2.902363
H	3.094052	-2.559789	-0.768358
H	1.624879	-1.976306	-1.588452
H	3.703290	1.210344	-0.252623
H	2.278214	-0.958025	0.839291

Im2:

P	0.961308	-0.134446	0.067048
O	0.807985	1.352762	-0.654949
O	-0.750502	-0.444719	-0.480024
O	0.720905	-0.350009	1.539219
O	1.337403	-1.327400	-1.000154
H	0.485380	-1.650792	-1.316673
H	1.682971	1.745760	-0.553764
O	2.689287	0.190998	0.201784
H	2.846868	0.041225	1.136988
C	-3.033987	-0.961376	0.090819
O	-3.974858	-0.276147	-0.764074
C	-3.356138	0.933098	-1.228460
C	-2.391479	1.334808	-0.123256
C	-1.824908	-0.032842	0.320746
H	-3.554275	-1.204137	1.020782
H	-4.153502	1.653024	-1.419820
H	-2.814676	0.745596	-2.162111
H	-2.938196	1.806040	0.698684
H	-1.588518	1.989282	-0.450379
H	-2.701051	-1.883861	-0.387220
H	-1.516116	-0.027866	1.366514

Ts2:

P	0.472694	-0.002628	0.135781
O	0.618227	-0.492149	-1.413434
O	-1.721930	-0.514336	-0.308773
O	0.140815	1.416727	0.424999
O	0.058399	-1.210607	1.090798
H	-0.919669	-1.252633	0.832959
H	1.565987	-0.552171	-1.576219

O	2.126990	-0.097425	0.452452
H	2.355942	0.765704	0.806970
C	-4.083850	-0.072784	0.034322
O	-4.780413	-0.139445	-1.230672
C	-3.865805	0.252846	-2.267347
C	-2.875081	1.187998	-1.592753
C	-2.664461	0.489367	-0.224369
H	-4.673538	0.566227	0.700632
H	-4.456247	0.711819	-3.063166
H	-3.349984	-0.627116	-2.665027
H	-3.316563	2.181445	-1.464643
H	-1.925561	1.278507	-2.114605
H	-4.008572	-1.073760	0.462561
H	-2.404783	1.236614	0.539134

Im3:

P	1.100433	-0.096807	0.130727
O	2.419093	-0.250445	-0.854675
O	-2.268841	-0.980244	-1.217183
O	0.670446	1.338081	0.067186
O	0.196313	-1.252895	-0.144494
H	-1.362471	-1.155174	-0.865445
H	2.633180	0.638474	-1.150733
O	1.757294	-0.366261	1.620027
H	1.957608	0.496369	1.993595
C	-3.263427	0.118305	0.742725
O	-4.703469	0.016953	0.623998
C	-5.049508	0.009125	-0.764190
C	-3.911789	0.743988	-1.464799
C	-2.687552	0.259568	-0.678394
H	-3.038435	0.989389	1.361989
H	-6.022653	0.492941	-0.866429
H	-5.125504	-1.020747	-1.129746
H	-4.033421	1.823328	-1.351869
H	-3.818340	0.501519	-2.521648
H	-2.868309	-0.776589	1.222012
H	-1.864447	0.976020	-0.688951

