Supplementary Material (ESI) for *Physical Chemistry Chemical Physics*

Description of Pentacoordinated Phosphorus under an External Electric Field: which basis sets and semi-empirical methods are needed?

Enrique Marcos, Josep M. Anglada and Ramon Crehuet *

Theoretical and Computational Chemistry Group, Departament de Química Orgànica Biològica, Institut d'Investigacions Químiques i Ambientals de Barcelona, IIQAB -CSIC/ Jordi Girona 18, E-08034 Barcelona, Spain. Fax: +34 93 204 59 04; Tel: +34 93 400 61 11; *E-mail: rcsqtc@iiqab.csic.es

(Electronic Supplementary Information)

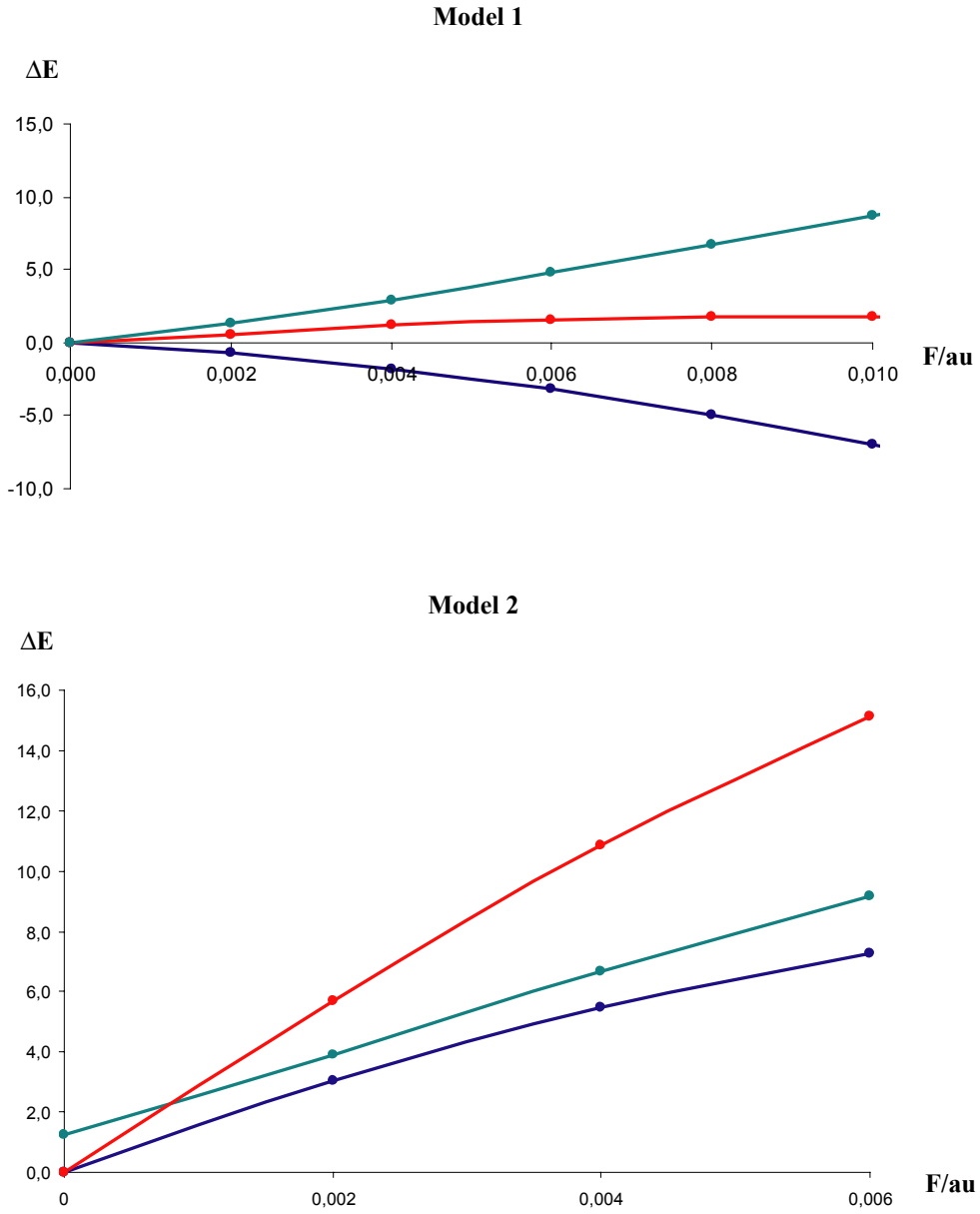

Figure S1. Variation of the energy of optimised structures with respect to the intensity of the electric field (F). Blue and red curves correspond to the intermediate and the transition state, respectively. The green straight line refers to the dependence of the energy barrier on the field. ΔE (in kcal·mol^{-1}) stands for the energy at a given field with respect to the energy at zero-field. These results have been obtained by means of the *m*PW1PW91 functional and the 6-31+G(d) basis set.

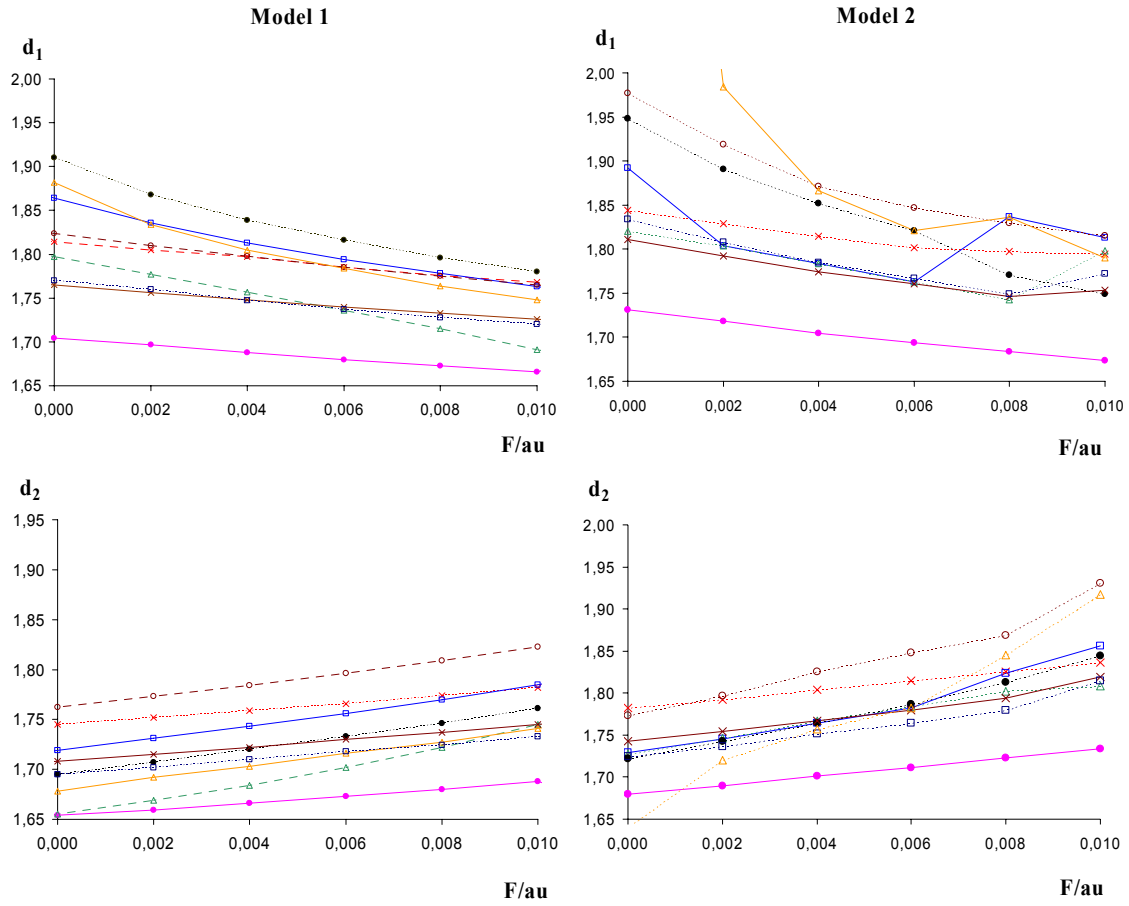

Fig. S2 Representation of the dependence of both apical bond distances (in Å) on the electric field (F) for models **1** and **2**, where d_1 corresponds to the weakest apical bond and d_2 the strongest one, for different semi-empirical methods (AM1: solid line with dots, PM3: dashed line with crosses, RM1: dashed line with triangles, AM1/Arantes: dashed line with squares, MNDO/d: dashed line with empty circles, AM1*: solid line with crosses, AM1/d-PhoT: solid line with triangles, PM6: solid line with squares). DFT results (dashed line with filled circles) are obtained by means of the *m*PW1PW91 functional and the 6-31+G(d) basis set.

Table S1. Calculation of the apical electric field (F) generated by the NAGK enzyme at the crystallographic position of the Aluminum atom using different QM/MM partitions. The different QM regions have included all the protein residues within a sphere of radius **r** and both the substrates and magnesium ion. The QM wave function has been computed by means of the AM1 semiempirical method and the corresponding Mulliken charges have been used to evaluate the contribution from this region to the total electric field.

r/Å	F/a.u.
0.0	0.0019
3.0	0.0021
4.0	0.0017
5.0	0.0018
6.0	0.0017
7.0	0.0017
8.0	0.0018

Table S2. Optimized apical bond distances (in angstroms) of the transition states of model reaction **1** for different electric fields (in a.u.).[a]

F	d_1	d_2
0.000	2.162	1.671
0.002	2.204	1.673
0.004	2.254	1.677
0.006	2.283	1.683
0.008	2.303	1.689
0.010	2.317	1.696

[a] The transition states have been computed at the *m*PW1PW91/6-31+G(d) level.

Table S3. Optimized cartesian coordinates for the intermediate and transition state of model reaction **1** at zero-field[a].

INTERMEDIATE				**TRANSITION STATE**			
	***m*PW1PW91/6-31+G(d)**				***m*PW1PW91/6-31+G(d)**		
O	-0.054651	1.449460	-0.668968	P	0.000000	0.000000	0.000000
P	0.113236	-0.009269	0.087789	O	0.000000	0.000000	1.670835
O	-1.796905	-0.006123	0.058374	O	0.533584	0.000000	-2.095186
O	1.781398	0.023601	-0.210514	O	-1.468885	-0.000193	-0.337903
O	0.146363	-0.166005	1.601431	O	0.896908	1.354253	-0.117268
O	-0.054576	-1.283192	-0.950435	O	0.897463	-1.353812	-0.117265
H	-1.017216	1.580228	-0.659694	H	1.043415	-1.369180	-1.091643
H	-1.016798	-1.415841	-0.965713	H	1.042838	1.369836	-1.091554
H	2.160450	-0.073874	0.670961	H	-0.335327	-0.000172	-2.513719
H	-1.998015	-0.093404	0.998510	H	-0.935792	0.000585	1.905414
	AM1				**AM1**		
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.670835	O	1.633900	0.000000	0.000000
O	0.533584	0.000000	-2.095186	O	-2.064000	0.404900	0.000000
O	-1.468885	-0.000193	-0.337903	O	-0.308800	-1.437100	0.138800
O	0.896908	1.354253	-0.117268	O	-0.362700	0.838800	-1.242600
O	0.897463	-1.353812	-0.117265	O	-0.121500	0.861600	1.368100
H	1.043415	-1.369180	-1.091643	H	-1.004100	1.134300	1.593400
H	1.042838	1.369836	-1.091554	H	-1.597000	0.894900	-0.994100
H	-0.335327	-0.000172	-2.513719	H	-2.501100	-0.404200	-0.222700
H	-0.935792	0.000585	1.905414	H	1.978200	-0.813300	0.349500
	RM1				**RM1**		
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.670835	O	1.618000	0.000000	0.000000
O	0.533584	0.000000	-2.095186	O	-2.050300	1.158600	0.000000
O	-1.468885	-0.000193	-0.337903	O	-0.377800	-1.442800	-0.000800
O	0.896908	1.354253	-0.117268	O	-0.262900	0.817000	-1.314900
O	0.897463	-1.353812	-0.117265	O	-0.265000	0.817700	1.312700
H	1.043415	-1.369180	-1.091643	H	-1.173200	1.261300	1.238100
H	1.042838	1.369836	-1.091554	H	-1.166600	1.261500	-1.247200
H	-0.335327	-0.000172	-2.513719	H	-2.817400	0.621100	0.008100
H	-0.935792	0.000585	1.905414	H	2.026700	-0.851700	-0.002600
	PM3				**PM3**		
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.746900	0.000000	0.000000	O	1.720300	0.000000	0.000000
O	-1.616100	0.825000	0.000000	O	-2.143100	1.702200	0.000000
O	-0.357600	-1.466100	0.013700	O	-0.430900	-1.422200	0.003100

O	0.022500	0.873200	-1.474500	O	-0.273000	0.873600	-1.380600
O	0.039600	0.914600	1.448400	O	-0.273000	0.874000	1.381000
H	-0.755100	1.437700	1.482600	H	-1.057200	1.442900	1.262400
H	-0.777900	1.387000	-1.516500	H	-1.056900	1.442900	-1.260300
H	-2.375200	0.270100	0.015200	H	-2.891600	1.136400	-0.000100
H	2.069100	-0.886200	-0.024100	H	2.064400	-0.877000	0.046100
		PM6				**PM6**	
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.719500	0.000000	0.000000	O	1.697500	0.000000	0.000000
O	-1.777400	0.540000	0.000000	O	-2.039000	0.873800	0.000000
O	-0.284600	-1.475200	0.010400	O	-0.383900	-1.440600	0.049100
O	0.035300	0.913200	-1.418800	O	-0.223300	0.891900	-1.340300
O	0.040400	0.934000	1.405100	O	-0.150000	0.894000	1.388800
H	-0.851100	1.336100	1.600900	H	-1.101000	1.304300	1.439500
H	-0.860500	1.300500	-1.624700	H	-1.301700	1.268200	-1.240400
H	-2.376700	-0.195900	0.006200	H	-2.682700	0.225300	-0.092800
H	2.081100	-0.904400	-0.004300	H	2.074600	-0.887800	0.156700
		MNDO/d				**MNDO/d**	
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.763200	0.000000	0.000000	O	1.684200	0.000000	0.000000
O	-1.732800	0.563300	0.000000	O	-2.065500	2.216800	0.000000
O	-0.255100	-1.494200	-0.003600	O	-0.525500	-1.401200	-0.007600
O	0.146400	0.861500	-1.465600	O	-0.221900	0.834400	-1.380400
O	0.149600	0.863400	1.461900	O	-0.243500	0.815500	1.393900
H	-0.425900	1.555200	1.740300	H	-0.804500	1.583500	1.504100
H	-0.423800	1.558300	-1.741700	H	-0.725600	1.644200	-1.470200
H	-2.444300	-0.047600	-0.012400	H	-2.997000	2.200300	-0.026300
H	2.236100	-0.811900	-0.052300	H	2.187800	-0.761900	0.240400
		AM1*				**AM1***	
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.708400	0.000000	0.000000	O	1.679100	0.000000	0.000000
O	-1.657800	0.602400	0.000000	O	-1.978500	0.792800	0.000000
O	-0.305700	-1.479800	0.017200	O	-0.457800	-1.429800	-0.027700
O	0.166800	0.860300	-1.433500	O	-0.176400	1.018200	-1.213500
O	0.175700	0.898400	1.408800	O	-0.040700	0.724500	1.500800
H	-0.631100	1.325600	1.726100	H	-0.928600	0.989100	1.791300
H	-0.639100	1.288900	-1.751300	H	-1.335000	1.308700	-1.044800
H	-2.312300	-0.095800	-0.000600	H	-2.666400	0.192800	-0.255500
H	2.052700	-0.899800	-0.022400	H	2.034400	-0.722500	0.535500
		AM1/Arantes				**AM1/Arantes**	
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.694800	0.000000	0.000000	O	1.666900	0.000000	0.000000
O	-1.747600	0.280400	0.000000	O	-2.072800	0.472700	0.000000
O	-0.165700	-1.532600	-0.060100	O	-0.296000	-1.444200	0.380000
O	-0.001300	0.891500	-1.412900	O	-0.203100	0.388400	-1.583800
O	-0.011800	0.780700	1.475600	O	-0.304000	1.183100	1.055100
H	-0.915200	1.025700	1.755600	H	-1.386700	1.228700	0.887600
H	-0.899400	1.183700	-1.663900	H	-1.134100	0.635300	-1.775100
H	-2.231900	-0.562500	-0.044300	H	-2.552000	-0.261900	0.411100
H	2.022500	-0.915800	-0.070300	H	2.011000	-0.905200	0.120100
		AM1/d-PhoT				**AM1/d-PhoT**	
P	0.000000	0.000000	0.000000	P	0.000000	0.000000	0.000000
O	1.679300	0.000000	0.000000	O	1.661000	0.000000	0.000000
O	-1.815400	0.471000	0.000000	O	-2.013700	0.565100	0.000000
O	-0.273400	-1.485200	0.011200	O	-0.328300	-1.467000	-0.019600
O	-0.011900	0.846900	-1.413100	O	-0.120700	0.885400	-1.357200
O	-0.005400	0.880700	1.392300	O	-0.128400	0.848300	1.379700
H	-0.909700	1.236800	1.597600	H	-1.082800	1.139700	1.520300
H	-0.919700	1.188000	-1.628100	H	-1.073600	1.182600	-1.495200

H	-2.385300	-0.315300	0.016600	H	-2.600200	-0.198300	-0.013800
H	2.005600	-0.929800	-0.010400	H	1.993100	-0.930000	-0.011100

[a] The geometry of both stationary points has been computed at different levels of theory.

Table S3. Optimized cartesian coordinates for intermediates and of model reaction **2** at zero-field[a].

INTERMEDIATE				**TRANSITION STATE**			
	***m*PW1PW91/6-31+G(d)**				***m*PW1PW91/6-31+G(d)**		
C	-2.431920	-0.216802	-0.321296	C	-2.619439	-0.243911	-0.270171
O	-1.486277	0.086044	0.515474	O	-1.679094	0.198177	0.478700
P	0.385769	0.067772	-0.022258	P	0.557212	0.130821	-0.086160
O	2.056021	0.455460	-0.186355	O	2.207528	0.429538	-0.091842
C	2.979191	-0.598576	-0.134501	C	3.070156	-0.685244	-0.054621
H	3.028570	-1.037709	0.872078	H	3.020773	-1.187903	0.919457
O	-3.624715	-0.261143	-0.043580	O	-3.799024	-0.426636	0.046487
O	0.056021	1.608862	-0.486044	O	0.214384	1.685490	-0.415053
O	0.243342	-1.103021	-0.947700	O	0.299428	-0.929714	-1.094875
O	0.590297	-0.131680	1.593771	O	0.469450	-0.190446	1.491468
H	2.717728	-1.387067	-0.850319	H	2.814674	-1.403090	-0.841500
H	-2.074791	-0.447596	-1.338818	H	-2.298970	-0.471671	-1.308599
H	-0.298103	-0.273901	1.957297	H	-0.502138	-0.244281	1.654267
H	0.913500	1.975183	-0.751156	H	1.068596	2.117979	-0.564907
H	3.965414	-0.189399	-0.384968	H	4.087534	-0.313867	-0.211514
	PM6				**PM6**		
P	0.0000	0.0000	0.0000	P	0.0000	0.0000	0.0000
O	1.7296	0.0000	0.0000	O	1.7052	0.0000	0.0000
O	-1.7367	0.7521	0.0000	O	-1.9095	0.6450	0.0000
O	-0.4172	-1.4282	-0.0605	O	-0.4073	-1.4340	0.0009
O	0.0329	0.8463	1.4501	O	0.0277	0.8505	-1.4411
O	0.1376	0.9085	-1.4123	O	-0.0692	0.9994	1.3200
C	2.3301	-0.9090	0.9205	C	2.2791	-0.7403	1.0810
C	-2.6992	0.2258	-0.7330	C	-2.9247	-0.1155	-0.3025
O	-3.8388	0.6784	-0.6667	O	-4.0846	0.2660	-0.1341
H	-2.4352	-0.6159	-1.3828	H	-2.6995	-1.1072	-0.7175
H	1.0760	1.0970	-1.6677	H	-0.9864	1.4326	1.4350
H	-0.8357	1.2958	1.6677	H	0.0832	0.2856	-2.2387
H	1.9260	-1.9231	0.7887	H	2.1214	-0.2087	2.0288
H	2.1736	-0.5565	1.9483	H	3.3482	-0.7735	0.8420
H	3.3960	-0.8879	0.6697	H	1.8711	-1.7602	1.1281
	MNDO/d				**MNDO/d**		
P	0.0000	0.0000	0.0000	P	0.0000	0.0000	0.0000
O	1.7733	0.0000	0.0000	O	1.7094	0.0000	0.0000
O	-1.8851	0.5946	0.0000	O	-2.3716	0.8732	0.0000
O	-0.3401	-1.4588	-0.0007	O	-0.4980	-1.4013	-0.0087
O	0.0658	0.9357	1.3893	O	-0.1217	0.9443	1.3474
O	0.0569	0.8283	-1.4518	O	-0.1102	0.8597	-1.3940
C	2.7524	-0.6192	0.7304	C	2.6758	-0.6735	0.7245
C	-3.0180	0.3419	-0.5937	C	-3.6296	0.8556	-0.2027
O	-4.0330	1.0039	-0.3195	O	-4.4095	1.7227	0.2556
H	-3.0513	-0.4825	-1.3475	H	-4.0477	0.0145	-0.8267
H	0.4483	1.6800	-1.5665	H	-0.9234	1.2406	1.7576
H	-0.6714	1.3046	1.8501	H	-0.3828	1.7623	-1.4758
H	2.6308	-1.7323	0.7974	H	3.6789	-0.4240	0.2928
H	2.8321	-0.2349	1.7825	H	2.5593	-1.7865	0.6814
H	3.7483	-0.4309	0.2449	H	2.6926	-0.3757	1.8043
	AM1/Arantes				**AM1/Arantes**		

P	0.0000	0.0000	0.0000	P	0.0000	0.0000	0.0000
O	1.7244	0.0000	0.0000	O	1.7060	0.0000	0.0000
O	-1.7648	0.4995	0.0000	O	-1.8760	0.4044	0.0000
O	-0.2786	-1.4980	-0.0224	O	-0.2653	-1.4991	0.1118
O	0.0130	0.7907	1.4591	O	-0.0065	0.6013	-1.5406
O	0.0972	0.7787	-1.4660	O	-0.0461	1.0231	1.2895
C	2.4962	-0.8650	0.8090	C	2.4595	-0.6666	0.9937
C	-2.7158	-0.0509	-0.7531	C	-2.9060	-0.4278	-0.0223
O	-3.8917	0.3428	-0.6480	O	-4.0605	-0.0027	0.1919
H	-2.4074	-0.8283	-1.4262	H	-2.6980	-1.4609	-0.2302
H	1.0161	0.9241	-1.7649	H	-0.9249	1.4339	1.4379
H	-0.8642	1.1175	1.7449	H	-0.1278	-0.0945	-2.2095
H	2.1718	-1.8894	0.6676	H	2.3577	-0.1433	1.9376
H	2.3934	-0.5719	1.8473	H	3.4857	-0.6290	0.6465
H	3.5202	-0.7382	0.4764	H	2.1257	-1.6935	1.0873
	AM1*				**AM1***		
P	0.0000	0.0000	0.0000	P	0.0000	0.0000	0.0000
O	1.7426	0.0000	0.0000	O	1.6818	0.0000	0.0000
O	-1.6461	0.7546	0.0000	O	-2.2557	1.0264	0.0000
O	-0.3843	-1.4459	-0.0698	O	-0.5713	-1.3662	0.1489
O	0.1199	0.7922	1.4615	O	-0.1137	1.0302	1.2701
O	0.1574	0.8972	-1.4031	O	-0.0623	0.7952	-1.4085
C	2.5820	-0.6395	0.9303	C	2.4856	-1.0127	0.5956
C	-2.5865	0.7999	-0.9468	C	-3.1281	1.5492	-0.7818
O	-3.6462	1.3664	-0.6411	O	-2.8173	1.8519	-1.9662
H	-2.3807	0.3495	-1.9395	H	-4.1551	1.7326	-0.3865
H	1.0637	1.0528	-1.7072	H	-1.0182	1.3138	1.5168
H	-0.7099	1.1259	1.8385	H	-0.9437	1.1620	-1.6923
H	2.3198	-1.7213	1.0593	H	2.7971	-0.6694	1.6158
H	2.5516	-0.1199	1.9230	H	1.9720	-2.0054	0.6603
H	3.6192	-0.5608	0.5058	H	3.3894	-1.0945	-0.0636

[a] The geometry of both stationary points has been computed at different levels of theory.