Electronic Supplementary Material (ESI) for RSC Advances.

Table S1. Parameters of the radial deformation functions $f(r) = [\zeta^{n+3}/(n+2)!] \times r^n \exp(-r\zeta)$

atoms	n (mr*)	ζ (bohr-1)	κ'	atoms	n	ζ (bohr-1)	κ'
P	6 (1) 7 (2) 8 (3)	5.1885	1.062(12)	both P	6 (1) 7 (2) 8 (3)	5.1885	1.083(11)
O1	2 (1) 2 (2) 3 (3)	4.4974	0.80(4)	O1A,O2A, O1B, O2B	2 (1) 2 (2) 3 (3)	4.4974	0.82(2)
O2, O3	2 (1) 2 (2) 3 (3)	4.4974	0.75	O3A, O4A, O3B, O4B	2 (1) 2 (2) 3 (3)	4.4974	0.75
O4	2 (1) 2 (2) 3 (3)	4.4974	0.96(4)				
O5, O6	2 (1) 2 (2) 3 (3)	4.4974	0.94(3)	O5A, O6A, O5B, O6B	2 (1) 2 (2) 3 (3)	4.4974	0.98(4)
N	2 (1) 2 (2) 3 (3)	3.8106	0.825(20)		2 (1) 2 (2) 3 (3)	3.8106	0.761(11)
all C	2 (1) 2 (2) 3 (3)	3.1303	0.894(10)		2 (1) 2 (2) 3 (3)	3.1307	0.925(11)
H	1 (1) 2 (2)	1.9154	1.2		1 (1) 2 (2)	1.9154	1.2

*) multipole rank

Table S2. Hirshfeld (Q_H) and Bader (Q_B) atomic charges. Subscripts *isol* and *cl* indicate the charges obtained for isolated molecules and clusters, respectively.

	Multipole refinements		DFT calculations			
I (NH_4H_2PEP)						
Atom	Q_H	Q_B	$Q_{B.isol}$	$Q_{H.isol}$	$Q_{B.cl}$	$Q_{H.cl}$
P	0.41	3.68	3.65	0.33	3.69	0.46
O1	-0.27	-1.48	-1.33	-0.25	-1.44	-0.23
H3	0.14	0.68	0.53	0.17	0.65	0.10
O2	-0.31	-1.49	-1.49	-0.47	-1.49	-0.30
O3	-0.34	-1.51	-1.51	-0.48	-1.47	-0.28
O4	-0.24	-1.39	-1.23	-0.16	-1.30	-0.15
C2	0.06	0.46	0.52	0.05	0.50	0.06
C3	-0.05	-0.05	-0.03	-0.13	-0.01	-0.10
H1	0.08	0.14	0.01	0.02	0.06	0.04
H2	0.06	0.15	0.02	0.03	0.05	0.03
C1	0.21	1.55	1.52	0.16	1.53	0.19
O6	-0.2	-1.15	-1.09	-0.15	-1.13	-0.15
O5	-0.23	-1.2	-1.10	-0.28	-1.16	-0.21
H4	0.13	0.68	0.54	0.15	0.65	0.10
N	-0.06	-1.19			-1.02	-0.04
H5	0.26	0.55			0.44	0.20
H6	0.17	0.55			0.50	0.12
H7	0.24	0.53			0.50	0.12
H8	0.27	0.57			0.47	0.18
II [$(NH_4)_2HPG$]						
P1A	0.13	3.42	3.65	0.30	3.68	0.42
P2B	0.11	3.38	3.68	0.30	3.71	0.42
O1A	-0.36	-1.49	-1.33	-0.27	-1.43	-0.27
O2A	-0.33	-1.46	-1.30	-0.20	-1.30	-0.16
O3A	-0.39	-1.45	-1.55	-0.54	-1.49	-0.35
O4A	-0.38	-1.46	-1.54	-0.52	-1.49	-0.34
O5A	-0.26	-1.15	-1.23	-0.45	-1.20	-0.25
O6A	-0.24	-1.07	-1.26	-0.49	-1.12	-0.25
O1B	-0.37	-1.53	-1.33	-0.26	-1.45	-0.27

O2B	-0.30	-1.45	-1.29	-0.20	-1.30	-0.16
O3B	-0.40	-1.42	-1.55	-0.54	-1.50	-0.37
O4B	-0.39	-1.47	-1.55	-0.53	-1.51	-0.34
O5B	-0.29	-1.15	-1.23	-0.45	-1.21	-0.26
O6B	-0.22	-1.06	-1.25	-0.48	-1.13	-0.25
C1A	0.11	1.45	1.58	0.05	1.56	0.15
C2A	-0.10	0.15	0.47	-0.04	0.47	-0.01
C1B	0.13	1.51	1.58	0.05	1.58	0.15
C2B	-0.11	0.12	0.45	-0.04	0.43	-0.01
H1A	0.17	0.69	0.51	0.14	0.64	0.09
H2A	0.08	0.18	-0.02	0.00	0.01	0.04
H20A	0.10	0.18	0.00	0.01	0.02	0.04
H1B	0.20	0.72	0.51	0.14	0.63	0.08
H2B	0.08	0.13	-0.02	0.00	0.03	0.05
H20B	0.05	0.13	0.00	0.01	0.05	0.05
N(av)	-0.024 (0.023)	-1.03 (0.023)			0.000 (0.005)	-0.99 (0.0979)
H(av)	0.23 (0.036)	0.5193 (0.030)			0.172 (0.071)	0.482 (0.017)

Table S3. Values of ρ_c (e·Å^{-3}) and $\nabla^2\rho_c$ (e·Å^{-5}) for ammonium dihydrogen phosphoenolpyruvate (I).

	experiment		theoretical, cluster		theoretical, free anion	
bond	ρ_c	$\nabla^2\rho_c$	ρc	$\nabla^2\rho_c$	ρ_c	$\nabla^2\rho_c$
P-O1	1.352(17)	16.03(6)	1.375	15.81	1.333	16.65
O1-H3	1.99(4)	-34.4(3)	1.98	-43.3	2.06	-38.2
P-O2	1.686(21)	20.12(8)	1.622	27.55	1.638	27.55
P-O3	1.609(21)	19.90(8)	1.591	25.69	1.604	25.81
P-O4	1.138(16)	10.70(6)	1.179	11.69	1.145	12.47
O4-C2	1.940(13)	-15.29(6)	1.898	-12.79	1.958	-15.41
C2-C3	2.399(17)	-24.92(5)	2.332	-22.91	2.334	-23.05
C3-H1	1.91(4)	-21.63 (13)	1.93	-26.03	1.91	-24.97

C3-H2	1.85(4)	-19.77(14)	1.92	-25.42	1.90	-24.80
C1-C2	1.840(12)	-15.56(4)	1.792	-14.85	1.774	-14.50
C1-O5	2.359(14)	-26.82(8)	2.310	-17.97	2.243	-14.19
O5-H4	1.92(4)	-30.6 (3)	1.91	-40.4	1.99	-36.8
C1-O6	2.882(19)	-30.30(11)	2.763	-12.83	2.800	-15.28
N-H5	2.17(7)	-34.5 (4)	2.24	-44.8		
N-H6	2.10(7)	-31.5(4)	2.24	-44.5		
N-H7	2.14(7)	-33.1(4)	2.25	-43.0		
N-H8	2.10(7)	-31.4(5)	2.25	-42.5		
hydrogen bonds						
H3...O3^{i}	0.41(3)	3.24(7)	0.47	2.47		
H4...O2^{ii}	0.47(3)	3.36(8)	0.52	2.533		
O3...H6	0.211(19)	1.89(4)	0.211	2.30		
O6-H7^{iii}	0.199(20)	1.73(4)	0.215	2.31		
O6-H5^{iv}			0.159	1.87		
symmetry codes: $^{i)}$ – x, 1/2-y, -1/2+z; $^{ii)}$ – 1/2+x, y, 3/2-z; $^{iii)}$ – x, 1/2-y, 1/2+z; $^{iv)}$ – 1-x; -1/2+y; 3/2-z						

Table S4. Values of ρ_c (e·Å^{-3}) and $\nabla^2\rho_c$ (e·Å^{-5}) for diammonium hydrogen phosphoglycolate (II)

	experiment		theoretical, clusters		theoretical, free anions	
bond	ρ_c	$\nabla^2\rho_c$	ρ_c	$\nabla^2\rho_c$	ρ_c	$\nabla^2\rho_c$
P1A-O1A	1.38(3)	14.99(8)	1.40	16.41	1.34	17.74
P1A-O2A	1.30(3)	10.40(8)	1.26	13.03	1.28	12.64
P1A-O3A	1.65(3)	15.89(9)	1.57	24.44	1.57	24.63
P1A-O4A	1.70(3)	17.04(9)	1.57	24.34	1.58	24.51
P2B-O1B	1.42(3)	14.95(8)	1.42	17.35	1.36	18.61
P2B-O2B	1.30(3)	11.90(8)	1.27	12.80	1.28	12.49
P2B-O3B	1.62(3)	15.73(9)	1.54	22.92	1.55	23.11
P2B-O4B	1.67(3)	18.23(10)	1.58	25.45	1.59	25.64
O1A-H1A	1.69(5)	-27.9(3)	1.79	-34.85	1.91	-32.12
O2A-C2A	1.700(19)	-8.88(6)	1.68	-11.65	1.67	-11.48

O5A-C1A	2.74(3)	-31.88(14)	2.63	-15.03	2.65	-16.19
O6A-C1A	2.60(3)	-31.43(13)	2.55	-19.18	2.52	-17.90
O1B-H1B	1.75(4)	-34.6(34)	1.80	-35.47	1.91	-32.85
O2B-C2B	1.676(19)	-8.21(6)	1.68	-11.37	1.68	-11.52
O5B-C1B	2.78(3)	-32.86(14)	2.63	-15.89	2.65	-17.05
O6B-C1B	2.58(3)	-30.96(13)	2.54	-19.06	2.52	-17.97
all N-H: min.	2.08(8)	-36.3(5)	2.22	-45.6		
max.	2.25(9)	-30.0(5)	2.26	-41.1		
av.	2.13(7)	-33.7(20)	2.24(1)	-43.3(13)		
C1A-C2A	1.771(17)	-13.73(5)	1.73	-14.33	1.73	-14.25
C2A-H2A	1.81(5)	-17.84(18)	1.88	-24.41	1.87	-24.15
C2A-H20A	1.81(5)	-19.22(16)	1.88	-24.39	1.87	-24.22
C1B-C2B	1.741(16)	-13.11(4)	1.73	-14.24	1.73	-14.12
C2B-H2B	1.81(5)	-18.64(15)	1.88	-24.32	1.87	-23.85
C2B-H20B	1.82(5)	-1766(17)	1.88	-24.51	1.87	-23.95
hydrogen bonds						
O3A-H31	0.23(3)	1.46(6)	0.22	2.31		
O3A-H24^{i}	0.23(6)	1.83(8)	0.24	2.14		
O4A-H13^{ii}	0.23(3)	2.38(5)	0.24	2.25		
O4A-H44^{iii}	0.27(3)	1.58(6)	0.28	2.57		
O5A-H12	0.22(3)	1.71(5)	0.22	2.21		
O5A-H43^{iv}	0.24(6)	2.34(10)	0.28	2.55		
O6A-H1A^{v}	0.59(3)	1.09(10)	0.52	2.59		
O3B-H34	0.29(3)	1.63(6)	0.29	2.58		
O3B-H21^{i}	0.16(6)	1.32(8)	0.17	1.76		
O4B-H41	0.25(3)	1.57(5)	0.23	2.27		
O4B-H14^{i}	0.27(7)	1.98(10)	0.28	2.60		
O5B-H23	0.19(3)	1.42(5)	0.18	1.99		
O5B-H33^{vi}	0.25(6)	2.03(9)	0.27	2.41		
O6B-H1B^{vii}	0.57(3)	0.20(11)	0.56	2.19		
symmetry codes: $^{i)}$ – 1-*x*, 1-*y*, 1-*z*; $^{ii)}$ – *x*, 3/2-*y*, -1/2+*z*; $^{iii)}$ – -1+*x*, *y*, *z*; $^{iv)}$ – 1-*x*, 2-*y*, 1-*z*; $^{v)}$ – *x*, 1+*y*, *z*; $^{vi)}$ – 1-*x*, -*y*, 1-*z*; $^{vii)}$ – *x*, -1+*y*, *z*						

Table S5. Additional topological data for ammonium dihydrogen phosphoenolpyruvate; the distances are in Å and the Hessian eigenvalues - in e·Å^{-5}.

	experiment							theoretical, cluster				theoretical, free anion			
bond	at1-at2	at1-CP	CP-at2	λ_1	λ_2	λ_3	ε	λ_1	λ_2	λ_3	ε	λ_1	λ_2	λ_3	ε
P-O1	1.5644	0.6333	0.9312	-8.83	-8.26	33.12	0.07	-10.910	-8.690	35.401	0.26	-10.709	-8.630	35.979	0.24
O1-H3	1.0301	0.7998	0.2303	-31.47	-30.98	28.04	0.02	-34.509	-34.100	25.304	0.01	-32.003	-31.377	25.207	0.02
P-O2	1.4921	.0.6140	0.8781	-11.59	-11.08	42.78	0.05	-10.401	-10.317	48.270	0.01	-9.991	-9.827	47.354	0.02
P-O3	1.4996	0.6180	0.8816	-10.87	-10.34	41.10	0.05	-10.160	-9.946	45.788	0.02	-9.835	-9.731	45.378	0.01
P-O4	1.6285	0.6563	0.9723	-6.50	-6.29	23.49	0.03	-7.601	-7.193	26.485	0.06	-7.186	-7.044	26.701	0.02
O4-C2	1.3711	0.8288	0.5434	-14.64	-14.09	13.44	0.04	-13.423	-13.045	13.676	0.03	-14.276	-13.633	12.500	0.05
C2-C3	1.3358	0.6896	0.6461	-19.08	-14.44	8.60	0.32	-18.014	-13.633	8.733	0.32	-18.120	-13.729	8.796	0.32
C3-H1	1.0903	0.7030	0.3872	-18.48	-17.15	14.00	0.08	-19.067	-18.833	11.876	0.01	-18.460	-18.052	11.548	0.02
C3-H2	1.0902	0.7111	0.3791	-17.85	-16.69	14.77	0.07	-18.725	-18.505	11.816	0.01	-18.414	-18.055	11.673	0.02
C1-C2	1.4967	0.7724	0.7243	-14.29	-11.55	10.29	0.24	-13.659	-11.642	10.447	0.17	-13.406	-11.440	10.346	0.17
C1-O5	1.3063	0.8227	0.4836	-20.73	-18.58	12.49	0.12	-19.725	-17.862	19.619	0.10	-18.963	-17.795	22.568	0.07
O5-H4	1.0501	0.8135	0.2366	-29.74	-29.41	28.52	0.01	-33.039	-32.533	25.135	0.02	-31.063	-30.292	24.508	0.03
C1-O6	1.2268	0.7932	0.4336	-28.10	-25.47	23.27	0.10	-25.304	-23.443	35.907	0.08	-25.328	-22.923	32.967	0.10
N-H5	1.0307	0.7649	0.2658	-29.00	-28.40	22.86	0.02	-33.039	-32.871	21.050	0.01				
N-H6	1.0302	0.7681	0.2621	-28.12	-27.36	24.02	0.03	-32.991	-32.919	21.392	0.00				
N-H7	1.0309	0.7690	0.2619	-28.54	-28.22	23.68	0.01	-32.316	-32.148	21.455	0.01				
N-H8	1.0301	0.7676	0.2625	-27.65	-27.10	23.35	0.02	-32.196	-31.569	21.282	0.02				
hydrogen bonds															
H3···O3^{i}	1.5358	0.4704	1.0654	-3.34	-3.25	9.83	0.03	-3.581	-3.468	9.521	0.03				
H4···O2^{ii}	1.4795	0.4464	1.0332	-4.08	-3.97	11.41	0.03	-4.196	-4.169	10.900	0.01				
O3···H6	1.8453	1.2025	0.6428	-1.32	-1.18	4.39	0.12	-1.163	-1.150	4.612	0.01				
O6-H7^{iii}	1.8658	1.2255	0.6402	-1.25	-1.22	4.20	0.02	-1.195	-1.177	4.678	0.02				
O6-H5^{iv}								-0.800	-0.752	3.422	0.06				

Symmetry codes aretaken from Table 4.

Table S6. Additional topological data for ammonium diammonium hydrogen phosphoglycolate; the distances are in Å and the Hessian eigenvalues - in e·Å^{-5}.

	experiment							theoretical, clusters				theoretical, free anions			
bond	at1-at2	at1-CP	CP-at2	λ_1	λ_2	λ_3	ε	λ_1	λ_2	λ_3	ε	λ_1	λ_2	λ_3	ε
P1A-O1A	1.5656	0.635	0.9306	-8.65	-8.43	32.07	0.02	-9.625	-8.811	34.847	0.09	-9.736	-8.856	36.341	0.10

P1A-O2A	1.6046	0.649	0.9556	-7.8	-7.16	25.36	0.07	-8.565	-8.165	29.762	0.05	-8.663	-8.102	29.400	0.07
P1A-O3A	1.5095	0.6228	0.8868	-10.85	-10.19	36.93	0.07	-10.177	-9.748	44.342	0.04	-9.970	-9.483	44.101	0.05
P1A-O4A	1.507	0.6199	0.887	-11.25	-10.46	38.75	0.08	-10.276	-10.032	44.655	0.02	-9.883	-9.683	44.077	0.02
P2B-O1B	1.5572	0.6337	0.9235	-8.86	-8.69	32.49	0.02	-9.832	-9.097	36.269	0.08	-10.090	-9.102	37.811	0.11
P2B-O2B	1.6029	0.6457	0.9572	-7.83	-7.34	27.08	0.06	-9.174	-7.965	29.931	0.15	-9.191	-7.945	29.617	0.16
P2B-O3B	1.5183	0.6242	0.8941	-10.71	-9.99	36.43	0.07	-10.081	-9.680	42.679	0.04	-9.786	-9.329	42.221	0.05
P2B-O4B	1.5029	0.6193	0.8837	-11.05	-10.59	39.87	0.05	-10.232	-10.158	45.860	0.01	-9.958	-9.760	45.354	0.02
O1A-H1A	1.0604	0.835	0.2254	-27.73	-26.27	26.05	0.05	-29.617	-29.304	24.072	0.01	-27.906	-27.352	23.132	0.02
O2A-C2A	1.4254	0.8444	0.581	-11.94	-11.16	14.21	0.08	-11.259	-10.963	10.575	0.03	-11.187	-10.849	10.553	0.03
O5A-C1A	1.2455	0.7968	0.4487	-26.2	-23.83	18.15	0.1	-23.877	-22.033	30.870	0.08	-23.904	-21.855	29.569	0.09
O6A-C1A	1.2675	0.8018	0.4657	-23.81	-22.05	14.43	0.08	-22.226	-20.508	23.552	0.08	-21.968	-20.766	24.822	0.06
O1B-H1B	1.0603	0.8402	0.2201	-30.31	-28.59	24.33	0.06	-30.268	-29.328	24.147	0.03	-28.461	-27.473	23.101	0.04
O2B-C2B	1.4213	0.8466	0.5747	-11.3	-10.82	13.91	0.04	-11.134	-10.893	10.661	0.02	-11.160	-10.960	10.596	0.02
O5B-C1B	1.2447	0.7903	0.4545	-26.32	-23.14	16.6	0.14	-23.901	-22.137	30.148	0.08	-23.959	-21.874	28.774	0.10
O6B-C1B	1.2683	0.8065	0.4619	-24.32	-21.85	15.2	0.11	-22.508	-20.236	23.687	0.11	-22.238	-20.327	24.605	0.09
all N-H: min. max. av.				-29.9 -27.0 -28.3(8)	-29.2 -26.8 -27.7(7)	20.8 23.8 22.3(8)	0.01 0.07 0.02(2)	-33.6 -31.8 -32.5(7)	-33.5 -31.1 -32.3(7)	21.1 21.7 21.(2)4	0.00 0.01 0.01(1)				
C1A-C2A	1.5148	0.7728	0.7421	-13.25	-11.21	10.73	0.18	-13.054	-11.741	10.464	0.11	-13.030	-11.724	10.507	0.11
C2A-H2A	1.1033	0.7333	0.37	-17.24	-16.36	15.76	0.05	-18.737	-17.729	12.057	0.06	-18.631	-17.611	12.095	0.06
C2A-H20A	1.1032	0.7019	0.4012	-16.86	-15.73	13.37	0.07	-18.780	-17.693	12.093	0.06	-18.727	-17.643	12.153	0.06
C1B-C2B	1.5157	0.7487	0.767	-12.98	-10.89	10.76	0.19	-13.086	-11.584	10.428	0.13	-13.018	-11.577	10.478	0.12
C2B-H2B	1.1036	0.6933	0.4104	-16.59	-15.59	13.53	0.06	-18.785	-17.715	12.182	0.06	-18.585	-17.392	12.122	0.07
C2B-H20B	1.1036	0.7197	0.3838	-17.11	-15.88	15.33	0.08	-18.879	-17.872	12.237	0.06	-18.599	-17.479	12.126	0.06
hydrogen bonds															
O3A-H31	1.8213	1.199	0.6222	-1.52	-1.41	4.39	0.07	-1.237	-1.203	4.750	0.03				
O3A-H24^{i}	1.8484	1.2085	0.6399	-1.42	-1.27	4.52	0.12	-1.306	-1.259	4.702	0.04				
O4A-H13^{ii}	1.8322	1.1965	0.6357	-1.35	-1.19	4.92	0.13	-1.351	-1.334	4.931	0.01				
O4A-H44^{iii}	1.7552	1.1666	0.5886	-2	-1.9	5.49	0.05	-1.689	-1.633	5.887	0.03				
O5A-H12	1.8361	1.2064	0.6298	-1.49	-1.42	4.61	0.05	-1.159	-1.107	4.473	0.05				
O5A-H43^{iv}	1.7776	1.1881	0.5895	-1.56	-1.44	5.33	0.09	-1.691	-1.659	5.897	0.02				
O6A-H1A^{v}	1.4364	1.015	0.4214	-5.6	-5.24	11.93	0.07	-4.143	-3.931	10.664	0.05				
O3B-H34	1.7602	1.1685	0.5917	-2	-1.76	5.38	0.13	-1.724	-1.671	5.972	0.03				
O3B-H21^{i}	1.9613	1.2917	0.6697	-1	-0.87	3.19	0.15	-0.816	-0.804	3.383	0.01				
O4B-H41	1.8216	1.1939	0.6277	-1.61	-1.47	4.64	0.1	-1.314	-1.300	4.880	0.01				
O4B-H14^{i}	1.7586	1.1763	0.5823	-1.81	-1.65	5.44	0.1	-1.620	-1.584	5.801	0.02				
O5B-H23	1.9423	1.2572	0.6851	-1.06	-1.04	3.52	0.02	-0.881	-0.808	3.675	0.09				
O5B-H33^{vi}	1.8043	1.184	0.6204	-1.55	-1.46	5.05	0.06	-1.632	-1.591	5.634	0.03				
O6B-H1B^{vii}	1.4532	1.0336	0.4196	-5.73	-5.3	11.23	0.08	-4.540	-4.482	11.208	0.01				

Symmetry codes are taken from Table 5.

Table S7. Results of the DFT calculations for organic phosphates R-O-PO_3H^-; in the table O refers to the ester oxygen atom

comp. nr.	R-	ΔE_h (kcal/mol)	*d(P-O)* (Å)	*d(C-O)* (Å)	*∠POC* (°)	*E(tlp)* (a.u.)	*E(dlp)* (a.u.)	*E[σ(P-O)]* (a.u.)	*E[σ(C-O)]* (a.u.)	*E[σ*(P-O)]* (a.u.)
1	HOOC-C(=CH_2)-	3.95	1.671	1.366	125.3	-0.29289	-0.51852	-0.69691	-0.85036	0.17361
2	CH_3-C(=O)-	7.74	1.699	1.359	126.9	-0.29784	-0.52959	-0.68983	-0.85202	0.14759
3	glucos-6-O-yl-	2.04	1.64	1.438	118.8	-0.2742	-0.54356	-0.69873	-0.74859	0.20573
4	CH_3-CH_2-C(=CH_2)-	5.18	1.657	1.383	127.1	-0.28485	-0.49827	-0.70369	-0.82626	0.19091
5	CH_2=CH-CH(-CH_3)-	1.86	1.635	1.466	119.6	-0.26957	-0.53696	-0.7043	-0.72111	0.21458
6	CH_3-C(=S)-	7.54	1.714	1.337	129.4	-0.30993	-0.51497	-0.67756	-0.9071	0.13238
7	CH_2OH-CHOH-CH_2-	1.58	1.64	1.439	119.1	-0.27462	-0.54215	-0.70001	-0.74737	0.20781
8	HOOC-CH_2-	1.47	1.654	1.419	116.3	-0.27562	-0.55944	-0.68441	-0.7682	0.19216
9	CH_3-	0.87	1.642	1.443	116.9	-0.26827	-0.54868	-0.69075	-0.73308	0.20464
10	CFH_2-	2.94	1.67	1.388	119.9	-0.28729	-0.5509	-0.69012	-0.80229	0.17563
11	$CClH_2$-	3.49	1.672	1.386	119.8	-0.28895	-0.5478	-0.68754	-0.81844	0.17401
12	$CBrH_2$-	3.82	1.678	1.376	120.4	-0.29147	-0.54389	-0.68464	-0.83529	0.16865
13	CF_3-	4.06	1.726	1.329	123.9	-0.3042	-0.5793	-0.65946	-0.89633	0.1207
14	CCl_3-	4.96	1.739	1.324	127.2	-0.30702	-0.5699	-0.6337	-0.9433	0.11099
15	CBr_3-	6.35	1.751	1.31	128.7	-0.3109	-0.56756	-0.61937	-0.96618	0.10032

Table S7 (continuation). P means population, Q_B(C) is the Bader charge of the ester C atom.

comp. nr.	*P(tlp).*	*P(dlp)*	*P[σ(P-O)]*	*P[σ(C-O)]*	*P[σ*(P-O)]*	*Q_B(C)*	*$\Sigma E^{(2)}$(tlp-PO_3H)* (kcal/mol)	*$\Sigma E^{(2)}$(tlp-R)* (kcal/mol)	*$\Sigma E^{(2)}$(dlp-PO_3H)* (kcal/mol)	*$\Sigma E^{(2)}$(dlp-R)* (kcal/mol)	*$\Sigma E^{(2)}$[σ(PO)-R]* (kcal/mol)
1	1.82742	1.94609	1.96791	1.98837	0.24583	0.4909	14.3	31.69	10.11	16.28	5.3
2	1.78305	1.9476	1.96937	1.99074	0.26611	1.4496	12.99	43.75	9.61	16.07	7.24
3	1.90244	1.95528	1.97101	1.98558	0.22571	0.4747	17.46	9.75	10.77	6.89	2.93
4	1.83452	1.94783	1.9715	1.98799	0.23874	0.4288	15.48	28.7	10.68	15.16	6.17
5	1.89911	1.95775	1.97241	1.98052	0.22159	0.4521	17.86	10.46	10.47	7.16	4.19
6	1.73486	1.94767	1.96077	1.99315	0.2765	0.3701	12.34	46.08	9.33	18.98	9.92
7	1.90236	1.95487	1.97164	1.98492	0.22596	0.4548	17.46	10.21	10.59	7.01	2.78
8	1.90717	1.95173	1.96802	1.98606	0.23579	0.4997	16.49	12.09	11.15	8.45	3.72

9	1.90739	1.95327	1.97218	1.98702	0.22873	0.4648	17.57	10.37	10.87	6.36	3.24
10	1.86538	1.95655	1.96942	1.99036	0.2445	1.0032	14.86	21.56	7.81	8.52	3.99
11	1.85091	1.95644	1.96786	1.99072	0.24646	0.6565	14.4	21.31	7.69	10.22	5.69
12	1.83386	1.95592	1.96674	1.99122	0.25033	0.5747	14.4	25	8.25	11.15	6.33
13	1.86299	1.93151	1.95001	1.99358	0.2863	2.2171	11.14	33.3	8.8	25.82	11.53
14	1.82192	1.91203	1.93437	1.99288	0.30197	1.003	9.33	35.77	12.29	24.39	12.35
15	1.8005	1.90145	1.92503	1.99164	0.3139	0.7011	9.01	40.38	14.53	32.13	16.82

Table S7 (continuation). E_{st} means steric repulsion energy, E_{st}(A-B) means steric repulsion energy between orbital A and fragment B, E_{st}(A) means steric repulsion energy obtained by orthogonalization of orbital A.

comp. nr.	$E_{st}(tlp)$ (kcal/mol)	$E_{st}(dlp)$ (kcal/mol)	$E_{st}(tlp\text{-}PO_3H)$ (kcal/mol)	$E_{st}(tlp\text{-}R)$ (kcal/mol)	$E_{st}(dlp\text{-}PO_3H)$ (kcal/mol)	$E_{st}(dlp\text{-}R)$ (kcal/mol)	$\rho_c(P\text{-}O)$ ($e\cdot Å^{-3}$)	$\nabla^2\rho_c(P\text{-}O)$ ($e\cdot Å^{-5}$)	$\rho_c(C\text{-}O)$ ($e\cdot Å^{-3}$)	$\nabla^2\rho_c(C\text{-}O)$ ($e\cdot Å^{-5}$)
1	1.29	-37.69	9.6	17.59	8.74	13.38	1.086935	7.564664	1.939616	-15.0893
2	0.47	-40.59	10.62	16.39	10.25	9.21	1.029786	5.698147	1.998559	-16.9934
3	8.4	-40.64	12.89	16.5	7.12	8.98	1.180151	9.360447	1.649303	-12.0743
4	2.44	-37.45	10.68	18.17	8.83	14.04	1.123338	8.26634	1.841687	-13.6203
5	13.61	-40.38	13.02	18.87	7.94	8.61	1.18972	9.769942	1.547583	-10.3184
6	-1.35	-37.39	8.75	17.85	8.97	14.77	0.991597	4.965449	2.075398	-15.8422
7	8.94	-39.23	12.74	17.9	7.43	9.82	1.180921	9.424863	1.640015	-11.8783
8	8.66	-38.08	12.94	17.18	8.58	8.1	1.149387	8.295239	1.735379	-13.6391
9	9.02	-38.77	13.41	16.43	7.26	8.5	1.187903	8.886825	1.612847	-11.3938
10	11.07	-39.54	11.8	15.54	7.21	9.43	1.110323	7.196515	1.889914	-16.7505
11	11.3	-38.64	12	18.28	7.44	9.73	1.102847	7.135743	1.881877	-15.972
12	10.82	-38.66	11.15	19.18	7.37	10.2	1.087649	6.820857	1.920027	-16.0324
13	12.69	-43.98	9.87	19.73	8.03	9.6	0.953602	4.759077	2.286634	-25.2104
14	14.01	-41.83	9.5	25.6	9.89	12.92	0.924649	4.126695	2.230387	-21.3719
15	14.01	-40.94	8.33	27.17	10.64	14.56	0.896688	3.696841	2.268181	-19.6662

Table S8. Results of the DFT calculations for the post-hydrolytic alcohols R-OH and the $H_2PO_4^-$anion.

comp. nr.	R-	*d(C-O)* (Å)	*E(tlp)* (a.u.)	*E(dlp)* (a.u.)	*E[σ(P-O)]* (a.u.)	*E[σ(C-O)]* (a.u.)
1	HOOC-C(=CH_2)-	1.370	-0.29072	-0.56664		-0.83417
2	CH_3-C(=O)-	1.354	-0.3026	-0.57766		-0.8459
3	glucos-6-O-yl-	1.431	-0.26819	-0.56683		-0.73635
4	CH_3-CH_2-C(=CH_2)-	1.377	-0.28194	-0.55454		-0.81306
5	CH_2=CH-CH(-CH_3)-	1.453	-0.26216	-0.56655		-0.71089
6	CH_3-C(=S)-	1.341	-0.31129	-0.56883		-0.88963
7	CH_2OH-CHOH-CH_2-*	1.435	-0.26403	-0.56755		-0.73003
8	HOOC-CH_2-	1.418	-0.27042	-0.57639		-0.75296
9	CH_3-	1.438	-0.26034	-0.56532		-0.7202
10	CFH_2-	1.379	-0.28751	-0.57309		-0.80064
11	$CClH_2$-	1.376	-0.29752	-0.56628		-0.81699
12	$CBrH_2$-	1.368	-0.30176	-0.56513		-0.83067
13	CF_3-	1.342	-0.31076	-0.609		-0.87219
14	CCl_3-	1.351	-0.31248	-0.60061		-0.90294
15	CBr_3-	1.343	-0.31536	-0.59412		-0.91958
	PO_3H-*				-0.71642	

Table S8 (continuation). P means population, E_{st} means steric repulsion energy, E_{st}(A) means steric repulsion energy obtained by orthogonalization of orbital A.

comp. nr.	*P(tlp).*	*P(dlp)*	*P[σ(P-O)]*	*P[σ(C-O)]*	*ΣE(2)(tlp-R)* (kcal/mol)	*ΣE(2)(dlp-R)* (kcal/mol)	*Est(tlp)* (kcal/mol)	*Est(dlp)* (kcal/mol)
1	1.85563	1.97624		1.99298	33.33	14.29	-3.76	-37.69
2	1.7995	1.97816		1.99666	45.89	12.43	-5.15	-40.59
3	1.95417	1.98189		1.9938	12.33	8.54	6.31	-40.64
4	1.86101	1.979		1.99331	31.32	13.07	-2.78	-37.45
5	1.95592	1.98126		1.98798	12.55	9.3	9.61	-40.38
6	1.75413	1.97589		1.99661	52.75	14.56	-5.57	-37.39
7*	1.957485	1.983635		1.99339	11.435	8.045	5.13	-39.23

8	1.95549	1.98208		1.9937	12.35	7.28	2.8	-38.08
9	1.96046	1.98511		1.99706	10.72	6.37	3.64	-38.77
10	1.89555	1.98228		1.99685	24.14	10.19	5.77	-39.54
11	1.87574	1.98055		1.99642	25.18	9.87	4.63	-38.64
12	1.85621	1.97974		1.99627	27.91	10.9	3.52	-38.66
13	1.8948	1.96024		1.99727	32.97	23.56	6.9	-43.98
14	1.8607	1.94969		1.99524	31.93	19.26	9.84	-41.83
15	1.84177	1.9425		1.99335	33.61	20.71	9.98	-40.94
$H_2PO_4^{-*}$			1.98228					

*) - Average values for two chemically equivalent O atoms have been taken.

Table S9. Selected statistical parameters related to steric repulsion (for convenience reasons only interactions above 0.5 kcal/mol have been taken into consideration).

repulsions	*mean* (kcal/mol)	*e.s.d.* (kcal/mol)	$R(d_{PO},x)$	$R(d_{CO},x)$	$R(d_{PO};x,E^{(2)}_C)$	$R(d_{CO};x,E^{(2)}_C)$
dlp-phosphate	8.38	1.16	0.714	-0.678	0.855	0.913
dlp-organic	10.79	2.40	0.576	-0.678	0.850	0.914
tlp-phosphate	11.15	1.68	-0.879	0.939	0.883	0.945
tlp-organic	18.83	3.29	0.731	-0.599	0.944	0.943

The correlation coefficients are shown as follows: $R(d_{PO},x)$ – the correlation coefficient between the P-O_e distance and the respective repulsion values; $R(d_{PO};x, E^{(2)}_C)$ – the multiple correlation coefficient between the P-O_e distance and the repulsion together with the sum of $\Delta E^{(2)}$ values related to the tlp-organic moiety interaction. The correlation coefficients involving the C-O_e distance are labeled analogically and *x* stands for the repulsion listed in the first column.

It is noteworthy that the steric repulsion of dlp is positively correlated with the P-O_e length, in other words this repulsion increases with the elongation of the bond. This is probably a result of concomitant increase of the C-O_e-P angle, which grows along with with shortening of C-O_e (**R**=-0.819) and with lengthening of P-O_e (*R*=0.760). N.B. a strong correlation between the angle and $\Sigma E^{(2)}(tlp\text{-}C)$ may be observed (*R*=0.926).

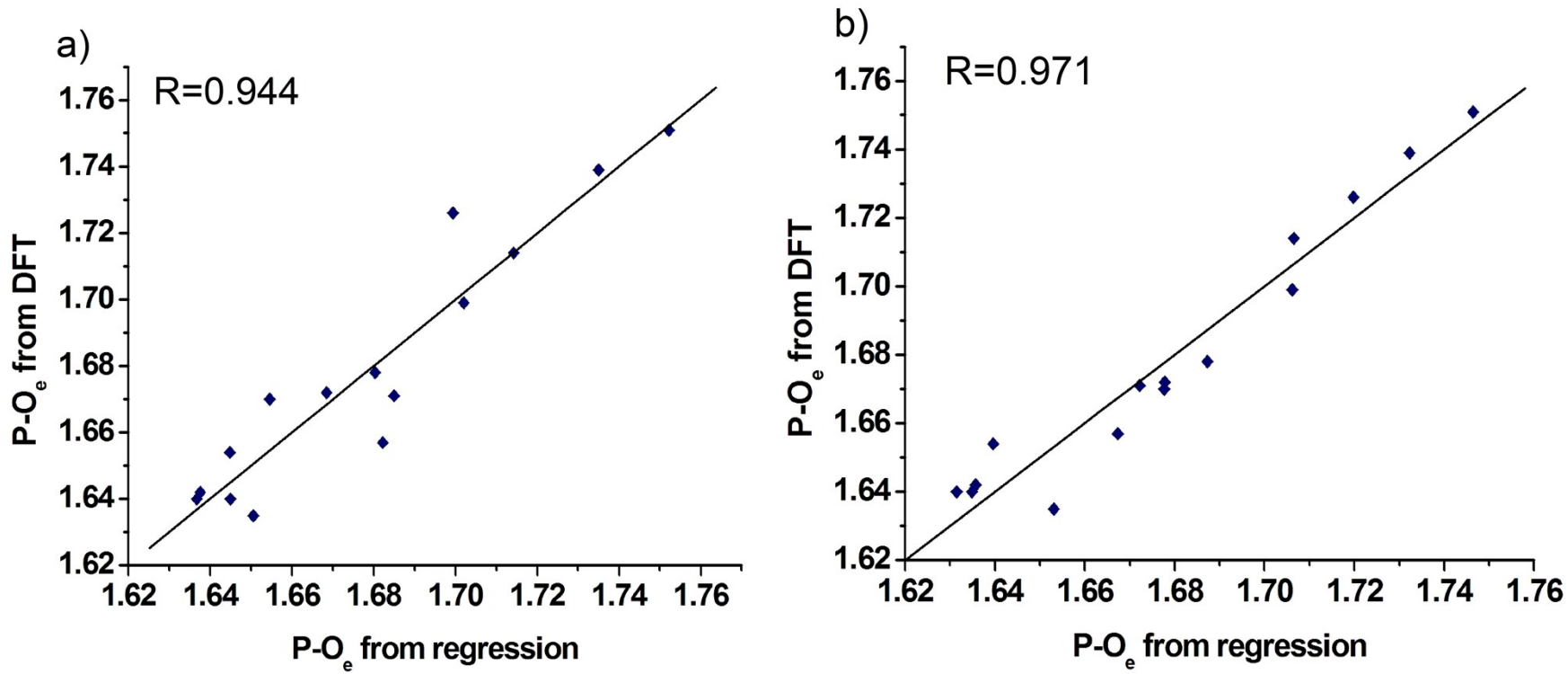

Fig. S1. Correlation of the P-O_e distances obtained from DFT and from linear regression: a) with the steric repulsion energy taken as the sum of the repulsions between tlp and the organic part of the ester, the regression equation is d_{PO} = 1.5311(212)+0.0019(4)·$\Sigma E^{(2)}$*(tlp-C)*+0.0053(13)·E_{st}*(tlp-C)*; b) with the repulsion energies obtained from orthogonalization of NLMOs, the regression equation is d_{PO} = 1.5701(89)+0.0031(3)·$\Sigma E^{(2)}$*(tlp-C)*+0.0037(6)·E_{st}*(tlp)*. The distances are in Å and the energy is expressed in kcal/mol.

Comparison of results obtained from the AUG-ATZ2P and TZ2P bases

Table S10. Comparison of selected parameters obtained from calculations applying the AUG-ATZ2P andTZ2P bases

comp. nr.	R-	ΔE_h (kcal/mol) AUG-ATZ2P	ΔE_h (kcal/mol TZ2P	$\Sigma E^{(2)}$(tlp-R) (kcal/mol) AUG-ATZ2P	$\Sigma E^{(2)}$(tlp-R) (kcal/mol) TZ2P
1	$HOOC-C(=CH_2)-$	4.03	3.95	30.05	31.69
2	$CH_3-C(=O)-$	6.99	7.74	38.75	43.75
3	glucos-6-O-yl-	2.71	2.04	10.61	9.75
4	$CH_3-CH_2-C(=CH_2)-$	4.79	5.18	27.78	28.7
5	$CH_2=CH-CH(-CH_3)-$	1.84	1.86	9.53	10.46
6	$CH_3-C(=S)-$	7.94	7.54	45.96	46.08
7	$CH_2OH-CHOH-CH_2-$*	2.55	1.58	10.49	10.21
8	$HOOC-CH_2-$	2.37	1.47	12.28	12.09
9	CH_3-	0.11	0.87	10.53	10.37
10	CFH_2-	3.23	2.94	21.72	21.56
11	$CClH_2-$	2.71	3.49	21.37	21.31
12	$CBrH_2-$	3.63	3.82	24.53	25
13	CF_3-	4.77	4.06	32.86	33.3
14	CCl_3-	2.65	4.96	35.23	35.77
15	CBr_3-	7.27	6.35	40.6	40.38

TableS10 (continuation)

comp. nr.	R-	$Q_B(C)$ AUG-ATZ2P	$Q_B(C)$ TZ2P	$\rho_c(C\text{-}O)$ (a.u.) AUG-ATZ2P	$\rho_c(C\text{-}O)$ (a.u.) TZ2P
1	$HOOC-C(=CH_2)-$	0.4939	0.4909	0.28829	0.287421
2	$CH_3-C(=O)-$	1.4493	1.4496	0.294598	0.296156
3	glucos-6-O-yl-	0.4938	0.4747	0.24443	0.244402
4	$CH_3-CH_2-C(=CH_2)-$	0.4319	0.4288	0.27328	0.27291

5	CH_2=CH-CH(-CH_3)-	0.4629	0.4521	0.2393	0.229328
6	CH_3-C(=S)-	0.3701	0.3701	0.30838	0.307542
7	CH_2OH-CHOH-CH_2-*	0.4696	0.4548	0.24312	0.243025
8	HOOC-CH_2-	0.505	0.4997	0.25715	0.257157
9	CH_3-	0.4873	0.4648	0.23999	0.238999
10	CFH_2-	1.0283	1.0032	0.2809	0.280056
11	$CClH_2$-	0.6705	0.6565	0.27949	0.278865
12	$CBrH_2$-	0.5908	0.5747	0.28484	0.284519
13	CF_3-	2.217	2.2171	0.33739	0.338844
14	CCl_3-	1.0039	1.003	0.33024	0.330509
15	CBr_3-	0.6058	0.7011	0.33572	0.33611

Table S10 (continuation)

comp. nr.	R-	$Q_B(C)$ AUG-ATZ2P	$Q_B(C)$ TZ2P	$\nabla^2\rho_c(C\text{-}O)$ (a.u.) AUG-ATZ2P	$\nabla^2\rho_c$(C-O) (a.u.) TZ2P
1	HOOC-C(=CH_2)-	-0.62358	-0.62614	1.365	1.366
2	CH_3-C(=O)-	-0.70415	-0.70516	1.362	1.359
3	glucos-6-O-yl-	-0.49832	-0.50103	1.438	1.438
4	CH_3-CH_2-C(=CH_2)-	-0.56118	-0.56519	1.383	1.383
5	CH_2=CH-CH(-CH_3)-	-0.47927	-0.42817	1.448	1.466
6	CH_3-C(=S)-	-0.65572	-0.65739	1.337	1.337
7	CH_2OH-CHOH-CH_2-*	-0.49098	-0.4929	1.439	1.439
8	HOOC-CH_2-	-0.56116	-0.56597	1.419	1.419
9	CH_3-	-0.4766	-0.4728	1.442	1.443
10	CFH_2-	-0.6977	-0.69508	1.388	1.388
11	$CClH_2$-	-0.66212	-0.66277	1.386	1.386
12	$CBrH_2$-	-0.66192	-0.66528	1.376	1.376
13	CF_3-	-1.04397	-1.04613	1.332	1.329
14	CCl_3-	-0.88945	-0.88685	1.325	1.324
15	CBr_3-	-0.79083	-0.81607	1.309	1.31

Comparison of the quantities obtained from the calculations performed in both bases shows that vast majority of the parameters are similar or very similar. The most serious discrepancy is the difference between the energies of hydrolysis of $CCl_3OPO_3H^-$ (compound #14). The AUG-ATZ2P energy is distinctly lower than analogous energies of both $CFl_3OPO_3H^-$ (#13) and $CBr_3OPO_3H^-$ (#15). We have not been able to find a plausible cause for this anomaly and for this reason we have omitted the molecule from the fit presented in Fig.S4.

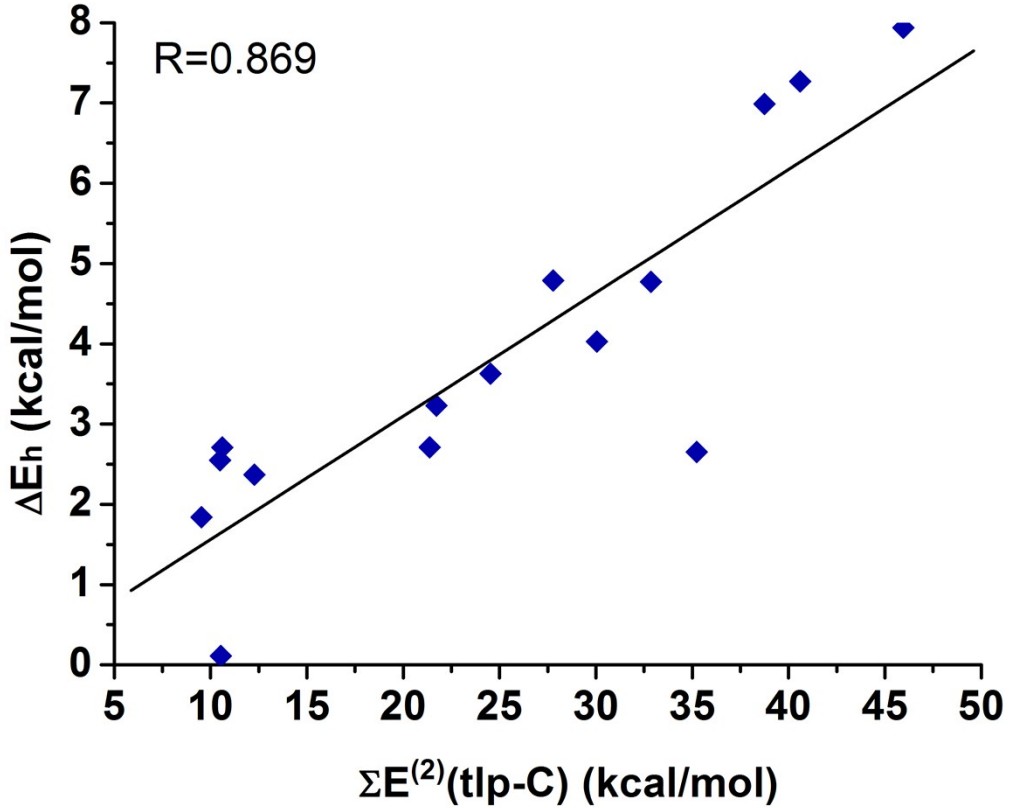

Fig. S2. Correlation of ΔE_h with $\sum E^{(2)}(tlp\text{-}C)$ taken from PW91, AUG-TZ2P, DFT calculations, the respective equation is: $\Delta E_h = 0.155(11)\ \sum E^{(2)}(tlp\text{-}C)$.

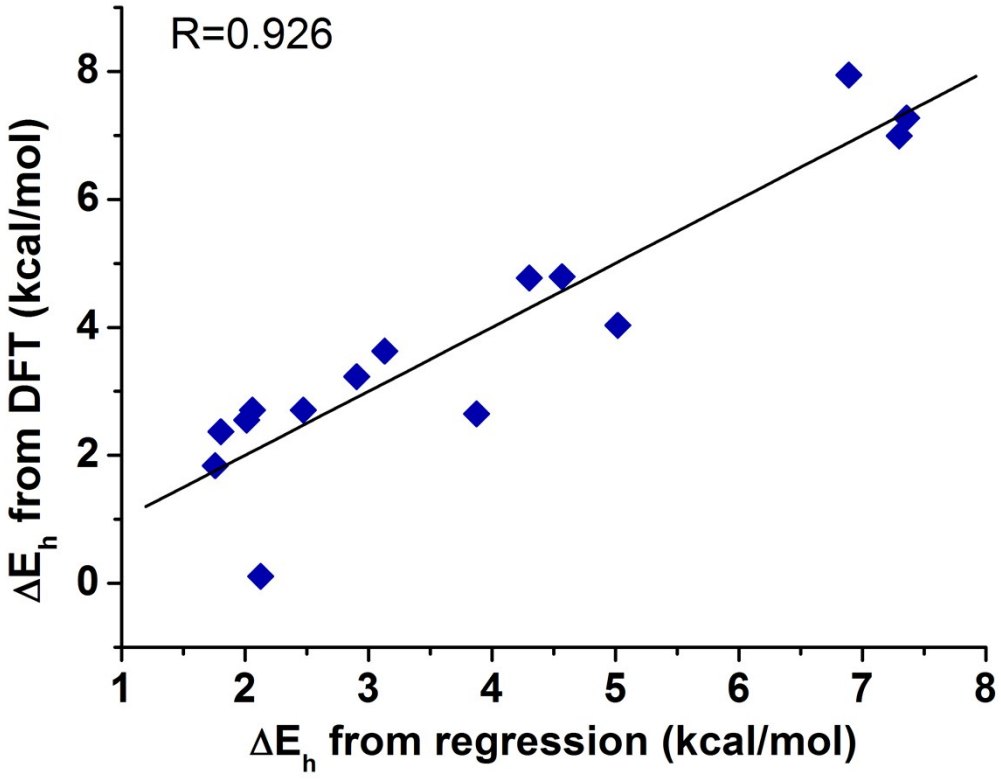

Fig. S3. Correlation of the hydrolysis energy obtained from DFT (PW91, AUG-TZ2P) and from linear regression against $\rho_c(C\text{-}O_e)$, $\nabla^2\rho_c(C\text{-}O_e)$ and $Q_B(C)$. The regression equation is: ΔE_h = 193(28)$\cdot\rho_c(C\text{-}O_e)$ + 44.1(82)$\cdot\nabla^2\rho_c(C\text{-}O_e)$ + 4.8 (13)$\cdot Q_B(C)$-25.6(38). Atomic units are used for $\rho_c(C\text{-}O_e)$ and $\nabla^2\rho_c(C\text{-}O_e)$.

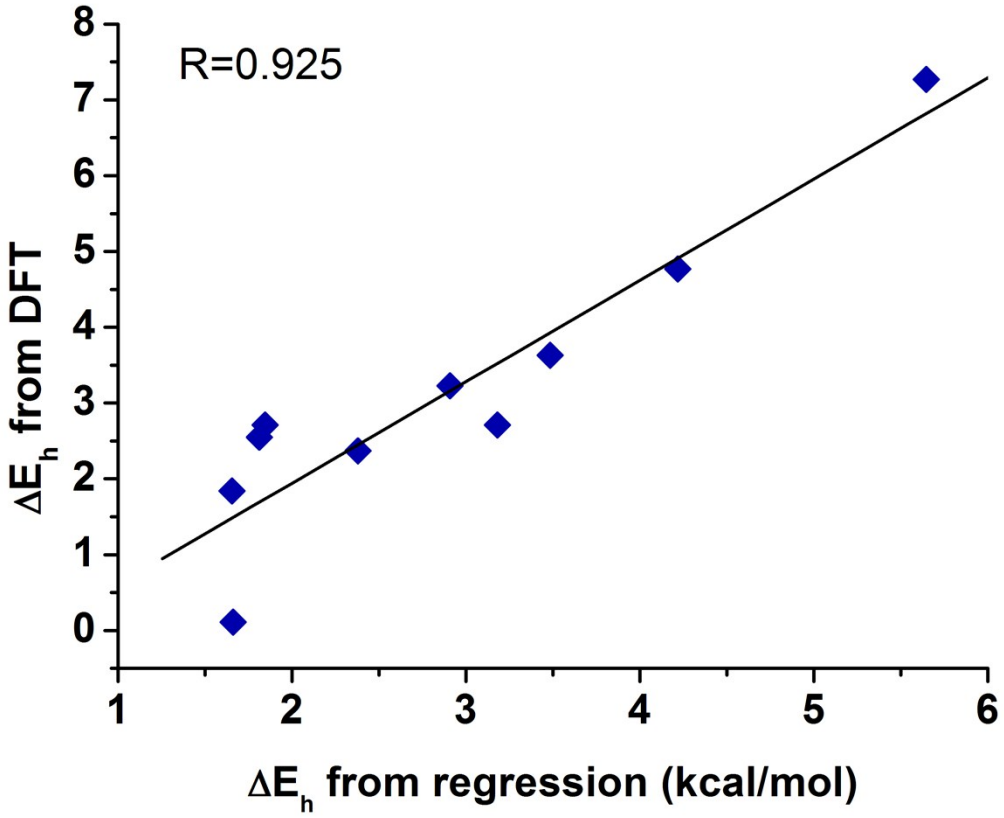

Fig. S4. Correlation of the hydrolysis energy obtained from DFT (PW91, AUG-TZ2P) and from linear regression against $\rho(C\text{-}O_e)$ and $Q_B(C)$ after elimination molecules with a double bond at the ester carbon atom and $CCl_3OPO_3H^-$. The regression equation is:
$\Delta E_h = 58.5(99)\cdot\rho_c(C\text{-}O_e) - 1.44(69)\cdot Q_B(C) - 11.8(25)$. Atomic units are used for $\rho_c(C\text{-}O_e)$.

The ΔE_h calculated for H_2PEP and HPG^{2-} (molecule A and B), analogously as it is presented in the main body text, are 4.1, 2.7 and 2.6 kcal/mol.

Statistical assessment of the correlation and regression results

Correlation coefficients

For all correlation coefficients, calculated in this work the *p*-value is less than 0.0011 based on the *t*-test ($t = R/[(1\text{-}R^2)/(N\text{-}2)]^{1/2}$)

t-Test of the parameters obtained from the linear regressions

It was intended to find relations, wherein the absolute values of the parameters were 3 times the e.s.d. or more. In fact, all, save one, parameters have the $|t|$ values greater than 2.95 and the *p* values 0.01 in the worst case. The only exception is the first coefficient in the equation in the caption of Fig. 10, for which $t = 2.0$ and $p = 0.035$.