Supporting Information

TABLE S1: Aliphatic and aromatic carboxylic acids

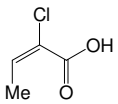
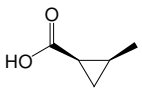
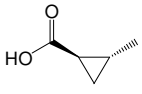
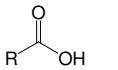
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
Aliphatic carboxylic acids	R-CH_2COOH				
acetic acid*	H	4.76 [3,4,7]; 4.757, 4.53, 4.48, 4.73(H_2O), 4.76, 4.75 [1]; 4.75 [6]; 4.637 [17]	-229.102690	-228.636660	292.44
bromoacetic acid*	Br	2.902, 2.889 (18℃), 2.856 (20℃) [2]; 2.92(H_2O), 2.901 [1]; 2.86 [7]; 2.90 [6]	-2803.344623	-2802.889378	285.67
butoxyacetic acid*	n-C_4H_9O	3.66 [7]	-461.519393	-461.057872	289.61
2-(butylthio)acetic acid*	S-n-C_4H_9	3.739 [1]	-784.521675	-784.059472	290.04
chloroacetic acid*[T]	Cl	2.866, 2.84(H_2O), 2.70 [1]; 2.821, 2.83, 2.861, 2.857, 2.855, 2.874, 2.867 [2];2.87 [6]; 2.86 [7]; 2.867 [8]	-688.726256	-688.271427	285.41
cyanoacetic acid*	CN	2.45, 2.456, 2.474, 2.466, 2.582 [2]; 2.50(H_2O), 2.471, 2.33 [1]; 2.47 [6]; 2.43 [7]; 2.46 [8]	-321.344507	-320.891028	284.56
ethoxyacetic acid*	OEt	3.652(18℃) [2, 6]; 3.84, 3.46 (20℃) [1]; 3.60 [7]; 3.65 [8]	-382.912899	-382.449448	290.82
fluoroacetic acid*	F	2.586, 2.662 [2]; 2.72 (H_2O), 2.584 [1]; 2.59 [6]; 2.66 [7]; 2.586 [8]	-328.340968	-327.885180	286.01
isopropoxyacetic acid*	$OCH(CH_3)_2$	3.72 [7]; 3.69 [2]	-422.218544	-421.756681	289.82
2-(isopropyithio)acetic acid [T]	$SCH(Me)_2$	3.72 [2]	-745.217690	-744.756158	289.62
methoxyacetic acid*	OCH_3	3.570, 3.57, 3.40, 3.31 (20℃), 3.36 (20℃) [1]; 3.53 [7]	-343.605752	-343.144737	289.29
2-(methylsulfonyl)acetic acid	SO_2CH_3	2.36 [2,7,8]	-817.027478	-816.572402	285.56
nitroacetic acid*	NO_2	1.48 (23.5℃) [1,6]; 1.68 [7,8]	-433.621525	-433.174229	280.68
2-oxoacetic acid (glyoxylic acid)* [T]	CHO	3.18 (20℃), 3.46, 2.98, 3.18 (20℃) [1]; 3.32 [9]; 3.46 [8]	-303.106658	-302.656163	282.69
phenylacetic acid*	C_6H_5	4.32, 4.312, 4.311, 4.305 [2]; 4.307, 4.305, 4.311, 4.33(H_2O), 4.20(31℃) [1]; 4.31 [6]; 4.312 [8]	-460.117511	-459.651507	292.42
phenoxyacetic acid	OC_6H_5	3.171, 3.125(18℃) [2]; 3.16, 3.182, 2.93, 2.96(31℃), 3.11(20℃), 3.12 [1]; 3.12 [7]; 3.171 [8]	-535.329329	-534.870622	287.84
2-(phenylsulfonyl)acetic acid*	$SO_2C_6H_5$	2.513[2]; 2.44 [7,8]	-1008.73311	-1008.276245	286.69
2-(phenylthio)acetic acid*	SC_6H_5	3.52 [7]; 3.568 [1]	-858.327313	-857.866972	288.87
propoxyacetic acid*	n-C_3H_7O	3.69 [7]	-422.215501	-421.755134	288.88
2-thiocyanatoacetic acid* [T]	SCN	3.58 [7]; 2.58 [6]	-719.547140	-719.094901	283.78
trans-2-chlorobut-2-ene carboxylic acid*		3.22[2]	-766.111518	-765.651479	288.68
cis-2-methylcyclopropane carboxylic acid*		5.02[1]	-345.780896	-345.310328	295.29
trans-2-methylcyclopropane carboxylic acid* [T]		5.00[1]	-345.784969	-345.315558	294.56
					
dichloroacetic acid*	$CHCl_2$	1.367, 1.301, 1.479, 1.234 [2]; 1.35 [6]; 1.35, 1.30 [1]; 1.26 [8]	-1148.347646	-1147.898764	281.68
tribromoacetic acid*	CBr_3	0.72 [1]; -0.147 [8]	-7951.808387	-7951.366290	277.42
trichloroacetic acid*	CCl_3	0.232, 0.217(20℃), 1.00 [2]; 0.512, 0.51, 0.518 (20℃) [1]; 0.52 [8]	-1607.959777	-1607.517191	277.73
trifluoroacetic acid* [T]	CF_3	0.588, 0.533 (35℃)[2]; 0.66 [6]; 0.52, 1.10 (22℃), 0.52 (20℃) [1]	-526.844241	-526.402707	277.07

TABLE S1 (cont.)

Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (Eh)	E_{anion} (Eh)	$\Delta E^{\$}$
pivalic acid	$C(CH_3)_3$	5.027 (18℃), 5.050, 5.025 (20℃) [2]; 5.04, 5.032, 5.03 (H_2O) [1]	-347.004521	-346.535386	294.39
butanoic acid (butyric caid)*	n-C_3H_7	4.939, 4.834, 4.819, 4.976 [2]; 4.83, 4.82 [1]; 4.82 [7]; 4.764 [17]	-307.707785	-307.239371	293.93
formic acid	H	3.76 [1]; 3.75 [6]; 3.77 [7]; 3.486 [17]	-189.787300	-189.328924	287.64
glycollic acid*	CH_2OH	3.836, 3.839, 3.885 [2]; 3.62, 3.83 (H_2O), 3.70 (30℃) [1]	-304.321352	-303.862155	288.15
mercaptoacetic acid * (thioglycolic acid)	CH_2SH	3.581, 3.677, 3.55, 3.42, 3.52(20℃) [1]; 3.68 [6]	-627.310403	-626.848954	289.56
3-methyl-2-butenoic acid* [T]	$CHC(CH_3)_2$	5.119, 5.121, 5.118, 5.137(18℃) [2]; 5.12 [1]	-345.795438	-345.324904	295.26
cyclohexanecarboxylic acid*	cyclohexyl	4.90, 4.914 [2]; 4.90, 4.89 [1]; 4.90 [8]	-424.414195	-423.944367	294.82
3-oxopropanecarboxylic acid*	CH_2CH_2CHO	3.45, 3.25 [1]	-381.732152	-381.266984	291.90
hexanoic acid (caproic acid)* [T]	n-C_5H_9	4.879, 4.849 (20℃), 4.845 (18℃) [2]; 4.88 [7]	-386.313651	-385.845189	293.96
pentanoic acid (valeric acid)*	n-C_4H_7	4.86, 4.939 (18℃), 4.835 (20℃) [2]; 4.763 (10℃), 4.861 (40℃),4.8 [1]; 4.87 [6]; 4.86 [7]; 4.56 [17]	-347.010764	-346.542265	293.99
α-keto-β-methylvaleric acid*	$COCH(CH_3)C_2H_5$	2.30[9]	-460.327285	-459.874191	284.32
propenoic acid (acrylic acid)*	$CH=CH_2$	4.247, 4.255, 4.26, 4.258 [2]; 4.25, 4.247, 4.246(20℃) [1], 4.25, 4.247 [1,8]	-267.178938	-266.714215	291.62
propargylic acid=2-propynoic acid	CCH	1.89 [8]; 1.84, 1.887 [2]	-265.924572	-265.473298	283.18
pyruvic acid = 2-oxo-propanic acid*	$COCH_3$	2.75 (18℃), 2.489, 2.42 (37℃) [2]; 2.39, 2.60, 2.105 [1]	-342.423953	-341.969377	285.25
acetopyruvic acid* [T]	$COCH_2COCH_3$	2.61 [9]	-495.059933	-494.604611	285.72
propanoic acid*	R_1, R_2=diH	4.872, 4.874, 4.879 (18℃) [2]; 4.875, 4.88, 4.86, 4.90, 4.69, 4.66(20℃), 4.89, 4.70 [1]; 4.87 [6]; 4.88 [7]; 4.878 [8]	-268.404978	-267.936625	293.90
2-bromopropanoic acid*	R_1=Br, R_2=H	2.791(18℃) [2]; 3.01 [1]	-2842.650137	-2842.191089	288.06
3-bromopropanoic acid* [T]	R_1=H, R_2=Br	3.991 (18℃) [2]; 4.01, 4.07 [1]	-2842.655255	-2842.192943	290.11
2-chloropropanoic acid* [T]	R_1=Cl, R_2=H	2.879 (18℃) [2]; 2.89 [1]; 2.84 [8]	-728.031992	-727.573465	287.73
3-chloropropanoic acid*	R_1=H, R_2=Cl	3.996, 4.097 (18℃) [2]; 4.08, 3.93 [1]; 3.99 [8]	-728.037568	-727.574262	290.73
2-hydroxypropanoic acid* (lactic acid)	R_1=OH, R_2=H	3.86 (18℃), 3.862, 3.856, 3.857 (24℃) [2]; 3.83 (31℃) [1]; 3.86 [8]	-343.627475	-343.167433	288.68
2-methylpropanoic acid* [T]	R_1=Me, R_2=H	4.64, 4.599 [1]	-307.705953	-307.236524	294.57
Dicarboxylic acids					
fumaric acid* (pKa1)	HOOC H	3.095 (H_2O) [1]; 3.02 (18℃), 3.02, 3.03 (18℃), 3.04(37℃)[2]; 3.02[6,7]; 3.10 [8]	-455.774554	-455.315474	288.08
fumaric acid (pKa2)	H COOH	4.602 (H_2O) [1]; 4.45 (18℃), 4.38, 4.47 (18℃), 4.51(37℃)[2]; 4.38[6,7]; 4.60 [8]	-455.315474	-454.848730	292.89
glutaric acid* (pKa1)	HOOC-$(CH_2)_3$-COOH	3.88, 4.0 [1]; 4.34, 4.35, 4.39 (20℃), 4.32 (18℃) [2]; 4.32 (18℃) [6]; 4.34 [7]; 3.77 [8]	-496.302208	-495.835022	293.16
glutaric acid (pKa2)		5.35, 5.79 [1]; 5.41, 5.42, 5.50 (20℃), 5.425 (18℃) [2]; 5.42 (18℃) [6]; 5.48 [7]; 6.08 [8]	-495.835022	-495.364872	295.02
maleic acid* (pKa1)	HOOC COOH	1.910 (H_2O), 1.92, 1.65 [1]; 2.00, 1.99 (37℃), 1.91 (18℃), 1.94 [2]; 1.92 [6,7]; 1.910 [8]	-455.764019	-455.312923	283.07
maleic acid (pKa2)	H H	6.332 (H_2O), 6.34, 5.61, 5.79 [1]; 6.26, 6.32 (37℃), 6.27 (18℃), 6.23, 6.29 (18℃) [2]; 6.23 [6,7]; 6.33 [8]	-455.312923	-454.838923	297.44

TABLE S1 (cont.)

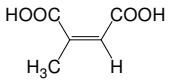
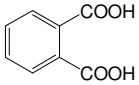
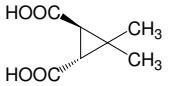
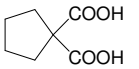
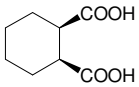
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
malonic acid* (pKa1)	HOOC-CH_2-COOH	2.847, 2.61, 2.87, 2.87 (H_2O), 2.30 (20℃), 2.851 (20℃), 2.849(20℃) [1]; 2.85, 2.83, 2.80 (18℃) [2]; 2.85 [6]; 2.83 [7]; 2.826 [8]	-417.689076	-417.241326	280.97
malonic acid (pKa2)		5.696, 5.27, 5.70,5.69 (H_2O), 5.70 (20℃), 5.683 (20℃) [1]; 5.67, 5.68 (20℃), 5.66, 5.69, 5.70 (18℃), 5.67 (18℃)[2]; 5.70 [6]; 5.69 [7]; 5.696 [8]	-417.241326	-416.760818	301.52
ethylmanolic acid* (pKa1)	HOOCCH(Et)COOH	2.96, 2.99 [2]; 2.99 [7]	-496.291667	-495.837353	285.09
ethylmanolic acid (pKa2)		5.83 [2, 7]	-495.837353	-495.357064	301.39
methylmalonic acid* [T] (pKa1)	HOOCCH(Me)COOH	3.05, 3.07, 3.12 (20℃) [2]; 3.05 [7]; 3.07 [8]	-456.989689	-456.529652	288.68
methylmalonic acid (pKa2)		5.87(20℃), 5.77[2]; 5.76[7]; 5.87 [8]	-456.529652	-456.055117	297.78
dimethylmalonic acid* (pKa1)	HOOC$(Me)_2$COOH	3.15, 3.17 [2]; 3.17 [7,8]	-496.288648	-495.827047	289.66
dimethylmalonic acid (pKa2)		6.06 [2,7,8]; 3.15 [2]	-495.827047	-495.352231	297.95
citraconic acid* (pKa1)		2.60, 2.2, 2.8 (20℃), 2.55 (20℃) [1]; 2.29 [7]	-495.076495	-494.627481	281.76
citraconic acid (pKa2)		6.1 (20℃), 6.30 (20℃) [1]; 6.15 [7]; 6.17 [2]	-494.627481	-494.146665	301.72
ethylmethylmalonic acid* [T] (pKa1)	HOOCC(Me)(Et)COOH	2.81, 2.86 [2]; 2.86 [7, 8]	-535.588147	-535.125095	290.57
ethylmethylmalonic acid (pKa2)		6.41 [2, 7, 8]	-535.125095	-534.650960	297.52
n-propylmalonic acid* (pKa1)		2.99, 3.00 [2]; 3.00 [7]; 2.97 [8]	-535.594710	-535.142082	284.03
n-propylmalonic acid (pKa2)	$CH_3(CH_2)_2CH(COOH)_2$	5.84 [2, 7, 8]	-535.142082	-534.659859	302.60
oxalic acid* (pKa1)	HOOC-COOH	1.525, 1.11, 1.13, 1.00, 1.20, 1.37, 1.08, 1.26, 1.32 [1]; 1.27, 1.25 (20℃), 1.30, 1.23, 1.34, 1.26 (30℃) [2]; 1.25 [6]; 1.23 [7]; 1.271 [8]	-378.373789	-377.925776	281.13
oxalic acid (pKa2)		3.85, 3.50, 3.63, 3.65, 3.67, 3.81, 3.55, 3.80 [1]; 4.29, 4.27 (20℃), 4.28, 4.27, 4.25 (20℃), 4.23 4.30, (20℃), 4.32 (32℃), 4.19 (18℃), 4.19 [2]; 3.81 [6]; 4.19 [7]; 4.271[8]	-377.925776	-377.457659	293.75
phthalic acid * (pKa1)		2.76, 2.63, 3.05 [1]; 2.95 [2]; 2.943 [6]; 2.95 [7,8]; 2.81 [5]	-609.399981	-608.951839	281.21
phthalic acid (pKa2)		4.92, 4.73, 4.89 [1]; 5.41 [2]; 5.432 [6]; 5.41 [7,8]; 5.24 [5]	-608.951839	-608.471160	301.63
succinic acid* (pKa1)	HOOC$(CH_2)_2$COOH	4.22, 4.21, 4.206, 3.98 [1]; 4.21, 4.22 (20℃), 4.16, 4.18, 4.20, 4.19, 4.22 (20℃), 4.21 (18℃), 4.18 (37℃), 4.20 (18℃), 4.18 (18℃) [2]; 4.21 [6]; 4.19 [7], 4.207 [8]	-456.998214	-456.532743	292.09
succinic acid (pKa2)		5.70, 5.72, 5.639, 5.20 [1]; 5.64, 5.64 (20℃), 5.61, 5.60, 5.48, 5.62 (18℃), 5.67 (20℃), 5.65 (37℃), 5.18(18℃), 5.64(18℃), 5.57 (18℃) [2]; 5.64 [6]; 5.48 [7]; 5.635 [8]	-456.532743	-456.062349	295.18
trans-caronic acid* (pKa1)		3.82, 3.599 [2]	-573.678991	-573.213369	292.18
trans-caronic acid (pKa2)		5.32, 5.252 [2]	-573.213369	-572.740402	296.79
cyclopentyl-1,1-dicarboxylic acid* (pKa1)		3.23 [2]	-573.689637	-573.235641	284.89
cyclopentyl-1,1-dicarboxylic acid (pKa2)		6.08 [2]	-573.235641	-572.751875	303.57
cis-cyclohexyl-1,2-dicarboxylic acid * (pKa1)		4.44, 4.25 [1]; 4.34 (20℃), 4.32 (19℃) [2]	-612.997932	-612.542820	285.59
cis-cyclohexyl-1,2-dicarboxylic acid (pKa2		6.89, 6.74 [1]; 6.77 (20℃), 6.76 (19℃) [2]	-612.542820	-612.056494	305.17

TABLE S1 (cont.)

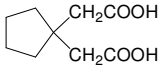
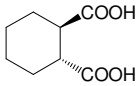
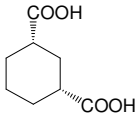
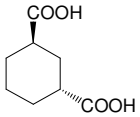
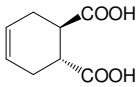
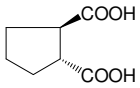
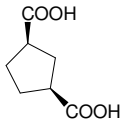
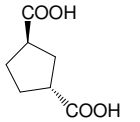
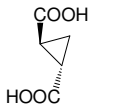
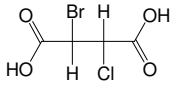
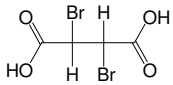
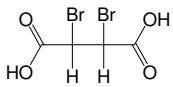
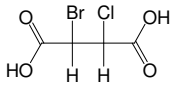
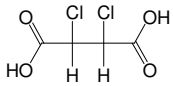
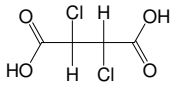
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
cyclopentyl-1,1-diacetic acid * [T] (pKa1)		3.80 [2]	-652.292277	-651.822206	294.97
cyclopentyl-1,1-diacetic acid (pKa2)		6.77 [2]	-651.822206	-651.348852	297.03
trans-cyclohexyl-1,2-dicarboxylic acid* [T] (pKa1)		4.30, 4.10 [1]; 4.18 (18℃) [2]	-613.004143	-612.534456	294.73
trans-cyclohexyl-1,2-dicarboxylic acid (pKa2)		6.06, 5.96 [1]; 5.93 (18℃) [2]	-612.534456	-612.063072	295.80
cis-cyclohexyl-1,3-dicarboxylic acid* [T] (pKa1)		4.10 (16℃) [2]	-613.005867	-612.538562	293.24
cis-cyclohexyl-1,3-dicarboxylic acid (pKa2)		5.46 (16℃) [2]	-612.538562	-612.067955	295.31
trans-cyclohexyl-1,3-dicarboxylic acid * (pKa1)		4.31 (19℃) [2]	-613.002149	-612.534340	293.55
trans-cyclohexyl-1,3-dicarboxylic acid (pKa2)		5.73 (19℃) [2]	-612.534340	-612.061536	296.69
trans-4-cyclohexyl-1,2-dicarboxylic acid* (pKa1)		3.89 [1]; 3.95 (20℃) [2]	-611.782300	-611.316863	292.07
trans-4-cyclohexyl-1,2-dicarboxylic acid (pKa2)		5.82 [1]; 5.81 (20℃) [2]	-611.316863	-610.845241	295.95
trans-cyclopentyl-1,2-dicarboxylic acid* [T] (pKa1)		4.14 (20℃) [1]; 3.96, 3.92 (18℃) [2]	-573.697003	-573.242763	285.04
trans-cyclopentyl-1,2-dicarboxylic acid (pKa2)		5.99 (20℃) [1]; 5.85, 5.91(18℃) [2]	-573.242763	-572.759656	303.15
cis-cyclopentyl-1,3-dicarboxylic acid* [T] (pKa1)		4.26, 4.23 (21℃) [2]	-573.698964	-573.231859	293.11
cis-cyclopentyl-1,3-dicarboxylic acid (pKa2)		5.51, 5.53 (21℃) [2]	-573.231859	-572.761512	295.15
trans-cyclopentyl-1,3-dicarboxylic acid * (pKa1)		4.32, 4.40 (22℃) [2]	-573.699641	-573.230281	294.53
trans-cyclopentyl-1,3-dicarboxylic acid (pKa2)		5.42, 5.45 (22℃) [2]	-573.230281	-572.761826	293.96
trans-cyclopropane-1,2-dicarboxylic acid* (pKa1)		3.80 (20℃) [1]; 3.65 (24℃) [2]	-495.074704	-494.611325	290.77
trans-cyclopropane-1,2-dicarboxylic acid (pKa2)		5.08 (20℃) [1]; 5.13 (24℃) [2]	-494.611325	-494.141420	294.87
threo-2-bromo-3-chlorosuccinic acid* (pKa1)		1.46 (20℃) [2]	-3490.858334	-3490.405436	284.20
threo-2-bromo-3-chlorosuccinic acid (pKa2)		2.77 (20℃) [2]	-3490.405436	-3489.947693	287.24
rac-2,3-dibromosuccinic acid* [T] (pKa1)		1.43 (20℃), 1.42 (20℃), 1.38 (18℃) [2]	-5605.476661	-5605.023626	284.28
rac-2,3-dibromosuccinic acid (pKa2)		3.24 (20℃), 3.09 (18℃) [2]	-5605.023626	-5604.565881	287.24
meso-2,3-dibromosuccinic acid* (pKa1)		1.56 (20℃), 1.51 (20℃), 1.45 (17℃) [2]	-5605.476699	-5605.023653	284.29
meso-2,3-dibromosuccinic acid (pKa2)		2.71 (20℃), 2.62 (19℃) [2]	-5605.023653	-5604.565766	287.33
erythro-2-bromo-3-chlorosuccinic acid* (pKa1)		1.43 (19℃) [2]	-3490.858207	-3490.405453	284.11
erythro-2-bromo-3-chlorosuccinic acid (pKa2)		2.60 (19℃) [2]	-3490.405453	-3489.947663	287.27
meso-2,3-dichlorosuccinic acid* [T] (pKa1)		1.44 (20℃), 1.52 (20℃), 1.49 (20℃) [2]	-1376.237585	-1375.785803	283.50
meso-2,3-dichlorosuccinic acid (pKa2)		3.03 (18℃), 2.94 (20℃), 2.97 (20℃) [2]	-1375.785803	-1375.329815	286.14
rac-2,3-dichlorosuccinic acid* (pKa1)		1.43 (16℃), 1.47 (20℃), 1.43 (20℃) [2]	-1376.240091	-1375.787613	283.93
rac-2,3-dichlorosuccinic acid (pKa2)		2.74 (16℃), 2.86 (20℃), 2.81 (20℃) [2]	-1375.787613	-1375.330162	287.06

TABLE S1 (cont.)

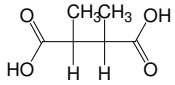
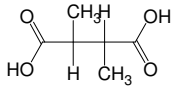
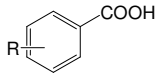
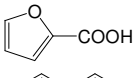
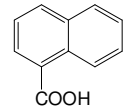
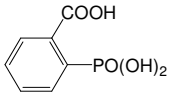
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
meso-2,3-dimethylsuccinic acid* (pKa1)		3.77 [2]	-535.595199	-535.126202	294.30
meso-2,3-dimethylsuccinic acid (pKa2)		5.94 [2]	-535.126202	-534.652603	297.19
rac-2,3-dimethylsuccinic acid* (pKa1)		3.94 [2]	-535.593264	-535.127341	292.37
rac-2,3-dimethylsuccinic acid (pKa2)		6.20 [2]	-535.127341	-534.652491	297.97
Aromatic carboxylic acids					
benzoic acid*	H	4.204, 4.185, 4.203, 4.222, 4.211, 4.201, 4.196, 4.213, 4.174, 4.218, 4.215, 4.199 [2]; 4.025, 4.024, 4.021, 4.022, 4.01, 3.99(20℃), 4.028 (20℃), 4.16(H_2O) [1] ; 4.199, 4.205, 4.204 [6]; 4.20 [7]; 4.26 [12]; 4.07 [13]; 3.98, 4.19 [15]; 4.68 [10]; 4.12 [5]	-420.817878	-420.353742	291.25
3-allyl-benzoic acid*	3-CH_2-CH=CH_2	4.32 [1]	-537.504225	-537.039953	291.34
3-bromobenzoic acid*	3-Br	3.812, 3.809 [2]; 3.813 [1]; 3.81 [6, 8]; 3.67 [5]	-2995.066108	-2994.604789	289.48
4-bromobenzoic acid* [T]	4-Br	3.971, 4.002[2]; 3.963[1]; 3.96[6]; 4.00[7]; 3.99[8]	-2995.067034	-2994.604546	290.22
4-butoxybenzoic acid*	4-n-C_4H_9O	4.53 [7]	-653.251915	-652.785236	292.85
3-chlorobenzoic acid* [T]	3-Cl	3.822, 3.83 [2]; 3.839, 3.82 [1]; 3.84 [6]; 3.83 [8]	-880.450237	-879.988753	289.59
4-chlorobenzoic acid*	4-Cl	3.983, 3.977, 3.986, 3.991 (20℃) [2]; 3.988 [1]; 4.00 [6]; 3.99 [8]	-880.451337	-879.988632	290.35
3-cyanobenzoic acid*	3-CN	3.60 [6]; 3.679, 3.602, 3.598 [2]	-513.068548	-512.608826	288.48
4-cyanobenzoic acid* [T]	4-CN	3.551, 3.548, 3.509 [2]; 3.55 [6, 8]	-513.068442	-512.608754	288.46
2-fluorobenzoic acid	2-F	3.267, 2.90 (17℃) [2]; 3.27 [6, 8]	-520.058885	-519.599157	288.48
3-flurobenzoic acid* [T]	3-F	3.865, 3.851 (16℃) [2]; 3.862 [1]; 3.87 [6, 8]	-520.067094	-519.605231	289.82
4-flurobenzoic acid*	4-F	4.141, 4.04 (15℃) [2]; 4.153 [1]; 4.15 [6]; 4.14 [8]	-520.068471	-519.605150	290.74
2-hydroxybenzoic acid (salicylic acid)	2-OH	2.754(30℃), 2.903 (30℃), 2.791 (19℃), 3.027 (18℃), 2.978 [2]; 2.98 [8]; 2.99, 2.82, 3.01 (H_2O), 3.15, 2.97, 2.70, 3.00, 2.93, 3.015 (20℃), 2.98 (20℃) [1]; 2.98 [7, 8]	-496.055221	-495.597665	287.12
3-hydroxybenzoic acid*	3-OH	4.079, 4.157 (18℃), 4.06 (19℃) [2]; 4.3, 4.08, 3.96 [1]; 4.08 [7, 8]	-496.052703	-495.588950	291.01
4-hydroxybenzoic acid [T]	4-OH	4.61 (27-28℃), 4.127 (19℃), 4.658 [2]; 4.582 [8]; 4.67, 4.50, 4.53, 4.36 (20℃) [1]; 4.58 [7]; 4.47[14]	-496.055747	-495.589595	292.52
2-methylbenzoic acid [T]	2-CH_3	3.908 [2]; 3.91 [6, 7]; 3.98(20℃), 3.93, 3.898 [1]	-460.118110	-459.650813	293.23
3-methylbenzoic acid*	3-CH_3	4.272 [2]; 4.25 [6]; 4.27 [7]; 4.254, 4.274, 4.29, 4.29(20℃) [1]; 4.269 [8]	-460.124663	-459.659959	291.61
4-methylbenzoic acid*	4-CH_3	4.373[2]; 4.37[6]; 4.34[7]; 4.373. 4.367, 4.41, 4.40(20℃), 4.37 [1]; 4.362 [8]	-460.125627	-459.660293	292.00
2-nitrobenzoic acid	2-NO_2	2.215, 2.173, 2.222 [2]; 2.17 [6, 7]; 2.21, 2.17(H_2O), 2.47(20℃) [1]	-625.335661	-624.882185	284.56
3-nitrobenzoic acid* [T]	3-NO_2	3.45, 3.493 [2]; 3.462, 3.473, 3.51 [1]; 3.45 [7]; 3.46 [6, 8]	-625.347533	-624.888592	287.99
4-nitrobenzoic acid*	4-NO_2	3.442, 3.425, 3.444 (20℃) [2]; 3.426, 3.422, 3.48 [1]; 3.43 [6]; 3.44 [7]; 3.441 [8]	-625.346832	-624.888118	287.85
2,4-dinitrobenzoic acid*	2,4-diNO_2	1.42 [2]	-829.858998	-829.411484	280.82
3-methoxybenzoic acid*	3-OCH_3	4.11(20℃), 4.088 [2]; 4.095, 4.086 [1]; 4.10 [6]; 4.09 [7]; 4.08 [8]	-535.335203	-534.871038	291.27
4-methoxybenzoic acid* [T]	4-OCH_3	4.52 (20℃), 4.411 [2]; 4.496, 4.511 [1]; 4.50 [6]; 4.47 [7]; 4.49 [8]	-535.338150	-534.871666	292.72
3-propoxybenzoic acid*	3-n-C_3H_7O	4.20 (20℃) [2, 7]	-613.946048	-613.481719	291.37

TABLE S1 (cont.)

Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
4-propoxybenzoic acid*	4-n-C_3H_7O	4.46 [7]; 4.78 (20℃) [2,8]	-613.949088	-613.482420	292.84
2,3,4,5-tetramethylbenzoic acid	2,3,4,5-tetraMe	4.22 [7]	-578.022340	-577.555034	293.24
2,4,6-trimethylbenzoic acid* ^{T}	2,4,6-triMe	3.446, 3.55, 3.394(20℃), 3.502(30℃) [1]; 3.43, 3.437 [2]	-538.726525	-538.256872	294.71
2,4,6-trinitrobenzoic acid*	2,4,6-triNO_2	0.65 [2]	-1034.369432	-1033.924689	279.08
protocatechuic acid*	3,4-diOH	4.48 [8,9]	-571.287046	-570.821030	292.43
2-furancarboxylic acid* ^{T}		3.272, 3.16 [1]; 3.15 [8]	-418.613778	-418.154430	288.25
naphthalene-1-carboxylic acid*		4.236 [2]; 3.69 [7,8]; 4.26 [11]	-574.43316	-573.967378	292.28
2-phosphonobenzoic acid		1.71 [2]	-988.553635	-988.107679	279.84

*A conformational search was carried out on these compounds using the GMMX feature of PCModel (see text for more details)

^{T} These compounds were in the internal test set for the combined mono- plus di-carboxylic acids; unmarked compounds were in the training set (see under Carboxylic acids in the Results and Discussion section)

$^{\$}$ kcal/mol

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TABLE S2: Phosphonic acids

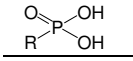
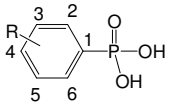
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
					
phosphonic acid (pKa1)	H	1.50 [16]	-568.938572	-568.488049	282.71
phosphonic acid (pKa2)		6.79 [16]	-568.488049	-568.006694	302.06
2-methylbutan-2-ylphosphonic acid* (pKa1)	$C(CH_3)_2CH_2CH_3$	2.88 [2]	-765.455017	-764.996394	287.79
2-methylbutan-2-ylphosphonic acid (pKa2)		8.96 [2]	-764.996394	-764.498972	312.14
iso-butylphosphonic acid* (pKa1)	Iso-C_4H_9	2.70 [2]	-726.162785	-725.705418	287.00
iso-butylphosphonic acid (pKa2)		8.43 [2]	-725.705418	-725.212543	309.28
n-butylphosphonic acid* (pKa1)	n-C_4H_9	2.59 [2]	-726.166562	-725.709223	286.98
n-butylphosphonic acid (pKa2)		8.19 [2]	-725.709223	-725.218436	307.97
t-butylphosphonic acid* (pKa1)	t-C_4H_9	2.79 [2]	-726.158298	-725.700804	287.08
t-butylphosphonic acid (pKa2)		8.88 [2]; 8.71 [15]	-725.700804	-725.205530	310.79
ethylphosphonic acid* (pKa1)	Et	2.45 [1]; 2.43, 2.45 [2]	-647.560186	-647.102968	286.91
ethylphosphonic acid (pKa2)		7.60, 7.85 [1]; 8.05, 7.85 [2]	-647.102968	-646.612252	307.93
methylphosphonic acid* (pKa1)	Me	2.12, 2.41, 2.48, 2.35 [1]; 2.38, 2.35 [2]	-608.260278	-607.804429	286.05
methylphosphonic acid (pKa2)		7.29, 7.35, 7.34, 7.1 [1]; 7.74, 7.1 [2]; 8.00 [15]	-607.804429	-607.317325	305.66
bromomethylphosphonic acid* (pKa1)	CH_2Br	1.14 [2]	-3182.498719	-3182.051451	280.67
bromomethylphosphonic acid (pKa2)		5.62 [2]	-3182.051451	-3181.569121	302.67
chloromethylphosphonic acid (pKa1)	CH_2Cl	1.51[1]; 1.40 [2]	-1067.880920	-1067.432422	281.44
chloromethylphosphonic acid (pKa2)		6.17 [1]; 6.30 [2]; 6.59 [15]	-1067.432422	-1066.943499	306.80
dichloromethylphosphonic acid* (pKa1)	$CHCl_2$	1.14 [1, 2]	-1527.498751	-1527.057592	276.83
dichloromethylphosphonic acid (pKa2)		4.97, 5.58 [1]; 5.61 [2, 15]	-1527.057592	-1526.576582	301.84
hydroxymethylphosphonic acid* (pKa1)	CH_2OH	1.91 [2]	-683.471485	-683.019675	283.52
hydroxymethylphosphonic acid (pKa2)		7.15 [2]	-683.019675	-682.534895	304.20
n-propylphosphonic acid* (pKa1)	n-C_3H_7	2.49 [2]	-686.863405	-686.405851	287.12
n-propylphosphonic acid (pKa2)		8.18 [2]; 8.17 [7]	-686.405851	-685.915522	307.69
iso-propylphosphonic acid* (pKa1)	iso-C_3H_7	2.66 [2]	-686.860039	-686.402012	287.42
iso-propylphosphonic acid (pKa2)		8.44 [2]	-686.402012	-685.908886	309.44
					
Phenylphosphonic acid* (pKa1)	H	1.83, 1.82 [2]	-799.967565	-799.514394	284.37
Phenylphosphonic acid (pKa2)		7.43 [1]; 7.07 [2]	-799.514394	-799.028424	304.95
phenol-3-phosphonic acid* (pKa1)	3-OH	1.78 [2]	-875.202346	-874.749536	284.14
phenol-3-phosphonic acid (pKa2)		7.03 [2]	-874.749536	-874.263981	304.69
2-bromophenylphosphonic acid* (pKa1)	2-Br	1.64 [2]; 1.53 [3]	-3374.208347	-3373.757849	282.69
2-bromophenylphosphonic acid (pKa2)		7.00 [2]; 7.37 [3]	-3373.757849	-3373.272755	304.40
2-chlorophenylphosphonic acid* (pKa1)	2-Cl	1.63 [2]; 1.56 [3]	-1259.593651	-1259.143185	282.67
2-chlorophenylphosphonic acid (pKa2)		6.98 [2]; 7.39 [3]	-1259.143185	-1258.658209	304.33
2-fluorophenylphosphonic acid* (pKa1)	2-F	1.64 [2]; 1.49 [3]	-899.214264	-898.764633	282.15
2-fluorophenylphosphonic acid (pKa2)		6.80 [2]; 7.19 [3]	-898.764633	-898.280222	303.97
2-methoxyphenylphosphonic acid* (pKa1)	2-OMe	2.16 [2]	-914.479668	-914.028649	283.02
2-methoxyphenylphosphonic acid (pKa2)		7.77 [2]	-914.028649	-913.540306	306.44
3-chloro-4-methoxyphenylphosphonic acid* (pKa1)	3-Cl, 4-OMe	2.25 [2]	-1374.116047	-1373.664133	283.58
3-chloro-4-methoxyphenylphosphonic acid (pKa2)		6.70 [2]	-1373.664133	-1373.17766	305.27
2-methylphenylphosphonic acid* (pKa1)	2-Me	2.10 [2]	-839.268941	-838.815133	284.77
2-methylphenylphosphonic acid (pKa2)		7.68 [2]	-838.815133	-838.325819	307.05
3-methylphenylphosphonic acid* (pKa1)	3-Me	1.88 [2]; 1.95 [3]	-839.274516	-838.820903	284.65
3-methylphenylphosphonic acid (pKa2)		7.44 [2]; 7.64 [3]	-838.820903	-838.334143	305.45

TABLE S2 (cont.)

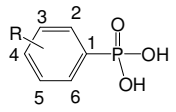
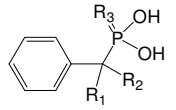
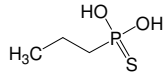
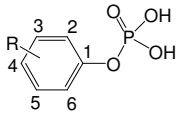
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
					
4-methylphenylphosphonic acid* (pKa1)	4-Me	1.84, 1.78 [2]; 2.00 [3]	-839.274346	-838.821108	284.41
4-methylphenylphosphonic acid (pKa2)		7.33, 7.24 [2]; 7.68 [3]	-838.821108	-838.334438	305.39
3-nitrophenylphosphonic acid* (pKa1)	3-NO_2	1.30 [2]; 1.20 [3]	-1004.495540	-1004.048855	280.30
3-nitrophenylphosphonic acid (pKa2)		6.27 [2]; 6.69 [3]	-1004.048855	-1003.565496	303.31
2-chloro-4-nitrophenylphosphonic acid* (pKa1)	2-Cl, 4-NO_2	1.12 [2]	-1464.119563	-1463.673512	279.90
2-chloro-4-nitrophenylphosphonic acid (pKa2)		6.14 [2]	-1463.673512	-1463.191703	302.34
4-sulfamoylphenyl-phosphonic acid* (pKa1)	4-SO_2NH_2	1.42 [2]	-1403.946884	-1403.497508	281.99
4-sulfamoylphenylphosphonic acid (pKa2)		6.38 [2]	-1403.497508	-1403.015318	302.58
2,6-dimethylphenylphosphonic acid (pKa1)	2, 6-diCH_3	2.39 [3]	-878.564671	-878.107790	286.70
2,6-dimethylphenylphosphonic acid (pKa2)		8.62 [3]	-878.107790	-877.618534	307.01
2-phosphono-benzoic acid (pKa2)	2-COOH	3.78 [2]	-988.107679	-987.640386	293.23
2-hydroxy-4-nitrophenylphosphonic acid (pKa1)	2-OH, 4-NO2	1.22 [4]	-1079.730965	-1079.287671	278.17
2-hydroxy-4-nitrophenylphosphonic acid (pKa2)		5.39 [4]	-1079.287671	-1078.816101	295.91
2-nitrophenylphosphonic acid (pKa1)	2-NO2	1.45; 1.28 [3]	-1004.482301	-1004.033185	281.82
2-nitrophenylphosphonic acid (pKa2)		6.74; 7.05 [3]	-1004.033185	-1003.547366	304.86
2-bromo-5-methylphenylphosphonic acid (pKa1)	2-Br, 5-Me	1.81 [2]	-3413.515203	-3413.064310	282.94
2-bromo-5-methylphenylphosphonic acid (pKa2)		7.15 [2]	-3413.064310	-3412.579113	304.47
2-methoxy-4-nitrophenylphosphoric acid (pKa1)	2-OMe, 4-NO2	1.53 [2]	-1119.011224	-1118.561699	282.08
2-methoxy-4-nitrophenylphosphoric acid (pKa2)		6.96 [2]	-1118.561699	-1118.077297	303.97
2,4-dimethylphenylphosphonic acid (pKa1)	2,4-diMe	2.17 [3]	-878.576393	-878.120717	285.94
2,4-dimethylphenylphosphonic acid (pKa2)		8.07 [3]	-878.120717	-877.631745	306.83
3,4-dimethylphenylphosphonic acid (pKa1)	3,4-diMe	2.04 [3]	-878.580392	-878.125297	285.58
3,4-dimethylphenylphosphonic acid (pKa2)		7.76 [3]	-878.125297	-877.638826	305.27
3-chlorophenylphosphonic acid (pKa1)	3-Cl	1.55 [2]; 1.53 [3]	-1259.599770	-1259.147992	283.50
3-chlorophenylphosphonic acid (pKa2)		6.65 [2]; 7.10 [3]	-1259.147992	-1258.664672	303.29
4-cyanophenylphosphonic acid (pKa1)	4-CN	1.27 [3]	-892.217959	-891.767540	282.64
4-cyanophenylphosphonic acid (pKa2)		6.79 [3]	-891.767540	-891.286162	302.07
2,4-dinitrophenylphosphonic acid (pKa2)	2,4-diNO_2	6.38 [15]	-1208.560176	-1208.078233	302.42
					
benzylphosphonic acid (pKa1)	R_1, R_2=diH; R_3=O	1.7 (17℃), 2.30 [1]	-839.274192	-838.819492	285.33
benzylphosphonic acid (pKa2)		7.4 (17℃), 7.55 [1]; 7.60 [5]; 7.72 [6]	-838.819492	-838.328893	307.86
(Fluorophenylmethyl)phosphonic acid (pKa2)	R_1=H, R_2=F, R_3=O	6.50 [5]; 6.60 [6]	-938.054442	-937.575678	300.43
[difluoro(phenyl)methyl)phosphonic acid (pKa2)	R_1, R_2=diF; R_3=O	5.71 [6]	-1037.315033	-1036.834236	301.70
phenylmethylphosphonothioic acid (pKa2)	R_1, R_2=diH; R_3=S	6.41 [7]	-1161.797324	-1161.317019	301.40
					
propylphosphonothioic acid (pKa2)		6.64 [7]	-1009.38489	-1008.904373	301.53
phosphoric acid (pKa1)	H_3PO_4	1.77 [9], 1.85 [10], 1.91 [11], 1.89 [12], 2.16 [13], 1.9 [14]	-644.204971	-643.756311	281.54
phosphoric acid (pKa2)		6.42 [9], 6.69 [10], 6.92 [11], 6.68 [12], 7.21 [13], 6.71 [14]	-643.756311	-643.275964	301.42

TABLE S2 (cont.)

Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
					
phenyl phosphate* (pKa1)	H	1.46 [1]	-875.204172	-874.760580	278.36
phenyl phosphate (pKa2)		6.29, 6.28[1]	-874.760580	-874.284476	298.76
4-chlorophenyl phosphate* (pKa1)	4-Cl	0.7 [1]	-1334.836750	-1334.394201	277.70
4-chlorophenyl phosphate (pKa2)		5.89, 5.83 [1]	-1334.394201	-1333.919162	298.09
2,4-dichlorophenyl phosphate* (pKa1)	2,4-diCl	0.6 [1]	-1794.463604	-1794.021918	277.16
2,4-dichlorophenyl phosphate (pKa2)		5.76, 5.68 [1]	-1794.021918	-1793.547567	297.66
2,4,5-trichlorophenyl phosphate (pKa1)	2,4,5-triCl	0.53 [1]	-2254.089459	-2253.648584	276.65
2,4,5-trichlorophenyl phosphate (pKa2)		5.47, 5.48 [1]	-2253.648584	-2253.176105	296.48
(2-phenylvinyl)phosphonic acid (pKa1)	ph-CH=CH-$PO(OH)_2$	2.00 [8]	-877.360119	-876.906435	284.69
(2-phenylvinylphosphonic acid (pKa2)		7.10 [8]	-876.906435	-876.422257	303.83

* A conformational search was carried out on these compounds using the GMMX feature of PCModel (see text for more details)

$ kcal/mol

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TABLE S3: Phenols, alcohols and thiols

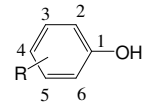
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
phenols					
		9.99, 9.998, 9.98, 9.88 (22℃), 9.92 (23℃), 9.94, 9.95, 9.90 [1]; 9.994, 10.202, 9.97, 9.86, 9.98, 9.78, 9.80, 9.78, 9.79, 10.00 (H_2O), 10.04 (20℃), 9.92 (20℃), 10.091 (20℃) [2]; 9.99 [13]; 9.92 [16]; 10.05			
phenol	H	[20]; 9.78 [21]; 9.92 [27]	-307.456558	-306.977335	300.72
2-aminophenol	2-NH_2	9.71 (22℃), 9.96 (20℃) [1]; 9.75, 10.05 (20℃) [2]	-362.816679	-362.334729	302.43
2-bromophenol*	2-Br	8.39, 8.42 [1]; 8.452, 8.44, 8.22, 8.33, 8.508 (20℃) [2]; 8.45 [13]; 8.42 [19]	-2881.704187	-2881.231846	296.40
2-tert-butylphenol*	2-$C(CH_3)_3$	10.623, 11.33, 11.16, 10.691 (20℃) [2] ; 10.62 [13]	-464.655257	-464.171229	303.73
2-chlorophenol*	2-Cl	8.11, 8.48 [1]; 8.527, 8.555, 8.48, 8.25, 8.53, 8.34 [2]; 8.56 [13]; 8.52 [16]; 8.57 [17]; 8.48 [19]	-767.087848	-766.615264	296.55
2,3-dichlorophenol*	2,3-diCl	7.696 [2]; 7.44 [3]; 7.71 [16]	-1226.715306	-1226.246580	294.13
2,4-dichlorophenol*	2,4-diCl	7.85 [1,3,19]; 7.892, 7.70 [2]; 7.90 [16]	-1226.719344	-1226.249846	294.61
2,5-dichlorophenol*	2,5-diCl	7.508[2]; 7.51 [3, 16]	-1226.720085	-1226.252564	293.37
2,6-dichlorophenol	2,6-diCl	6.786, 6.791, 6.81 [2]; 6.78 [3,16]	-1226.717007	-1226.251567	292.07
2,5-dimethylphenol*	2,5-diCH_3	10.22 (24℃), 10.3 (28℃) [1]; 10.41, 10.404, 10.46 (20℃), 10.472 (20℃) [2]; 10.32 [19]	-386.068274	-385.585475	302.96
2,6-dimethylphenol	2,6-diCH_3	10.59, 10.5 (28C) [1]; 10.65 (20℃), 10.615, 10.63, 10.59, 10.66 (20℃), 10.684 (20℃) [2]; 10.60 [19]; 10.57 [27]	-386.066553	-385.583604	303.06
2,4-dinitrophenol	2,4-diNO_2	4.09, 4.11, 4.089, 4.055 (28℃), 4.021 [1]; 4.073, 4.10, 3.93, 4.07, 4.12 (H_2O), 4.07 (H_2O), 4.06 (H_2O) [2]; 4.07 [13]; 4.14 [17]	-716.516646	-716.064783	283.55
2,5-dinitrophenol*	2,5-diNO_2	5.315 (18℃), 5.216 [1]; 5.21, 5.04, 5.212, 5.20 (H_2O), 5.19 (H_2O) [2]; 5.22 [17, 19]	-716.512436	-716.055150	286.95
2,6-dinitrophenol	2,6-diNO_2	3.706, 3.712, 3.713, 3.799 [1]; 3.695, 3.73 (H_2O) [2]; 3.78 [17]; 3.43 [18]	-716.505671	-716.053033	284.03
2-fluorophenol	2-F	8.81 [1, 19]; 8.70, 8.49, 8.73 [2]; 8.73 [13]	-406.702821	-406.229619	296.94
2-methoxyphenol*	2-OCH_3	9.98 [1, 13]; 9.98, 9.90, 9.86 [2]; 9.93 [19]	-421.971345	-421.489841	302.16
2-methylphenol (o-cresol)	2-CH_3	10.287, 10.15, 10.14 (23℃), 10.28, 10.27 (17℃) [1]; 10.22. 10.333, 10.32, 10.29, 10.10 [2]; 10.29 [13]; 10.28 [19]	-346.762109	-346.280651	302.12
2-nitrophenol*	2-NO_2	7.216, 7.234, 7.092, 7.229 [1]; 7.22, 7.21, 7.25, 7.06, 7.08, 7.04, 7.22 (H_2O), 7.230, 7.293 (20℃) [2]; 7.23 [13, 19]	-511.988406	-511.522447	292.39
2,3,4-trichlorophenol	2, 3, 4-triCl	6.97 [16]; 7.10 [28]	-1686.341043	-1685.874696	292.64
2,4,5-trichlorophenol*	2, 4, 5-triCl	7.37 [3]; 6.72 [16]; 7.07 [28]	-1686.345798	-1685.880762	291.81
2,4,6-trimethylphenol*	2, 4,6-triCl	10.88 [1]; 10.86, 10.89, 10.99 (20℃) [2]; 10.88 [3]; 10.55 [19]	-425.371884	-424.886852	304.36
2,4,6-trinitrophenol	2, 4, 6-triNO_2	0.6, 0.381, 0.196, 0.29 [1]; 0.33, 0.373, 0.27 (20℃) [2]	-921.027773	-920.587147	276.50
2,3,4,6-tetrachlorophenol	2, 3, 4, 6-tetraCl	5.62 [1]; 5.22 [16]	-2145.967683	-2145.508343	288.24
pentachlorophenol	2, 3, 4, 5, 6-pentaCl	4.90 [1]	-2605.586685	-2605.130120	286.50
3-aminophenol*	3-NH_2	9.87 (22℃) [1]; 9.86, 9.96 (20℃) [2]	-362.820136	-362.337644	302.77
4-aminophenol	4-NH_2	10.3 [1]; 10.46, 10.44 [2]	-362.815689	-362.329414	305.14
3-bromophenol*	3-Br	8.87 [1]; 9.031, 9.03, 9.00, 8.75, 9.06, 9.099 (20℃) [2]; 9.03 [13]; 9.11 [19]	-2881.706088	-2881.232667	297.08

TABLE S3 (cont.)

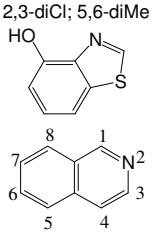
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
4-bromophenol	4-Br	8.25, 9.34 [1]; 9.366 (23.6℃), 9.36, 9.06, 9.17, 9.35 (H_2O) [2]; 9.37 [13]; 9.12 [18]; 9.38 [19]; 9.20 [21]	-2881.705919	-2881.230354	298.42
3-tert-butylphenol	3-$C(CH_3)_3$	10.119, 10.08, 10.194 (20℃) [2]; 10.12 [13]	-464.662249	-464.180744	302.15
4-tert-butylphenol*	4-$C(CH_3)_3$	10.390, 10.23, 10.25 (20℃) [2]; 10.23 [13]; 10.14 [21]	-464.661819	-464.180362	302.12
3-chlorophenol*	3-Cl	9.13 [1]; 9.13, 9.08, 8.76, 8.80, 9.119, 9.180 (20℃), 9.13 [2] ; 9.12 [13]; 8.79 [16]; 9.10 [17]; 8.88 [18]; 9.02 [19]; 8.99 [27]	-767.090259	-766.616113	297.53
4-chlorophenol	4-Cl	9.38 [1]; 9.406, 9.38, 9.42, 9.35, 9.16, 9.10, 9.42 [2]; 9.41 [13]; 9.37 [16]; 9.44 [17]; 9.25 [18]; 9.38 [19]; 9.37 [27]	-767.089813	-766.613707	298.76
3-cyanophenol	3-CN	8.608, 8.57, 8.34 [2]; 8.61 [13]; 7.83 [21]	-399.709861	-399.2383816	295.86
4-cyanophenol	4-CN	7.95 [1, 19]; 7.967, 7.97, 7.85, 7.71 [2]; 7.97 [13]	-399.712848	-399.245768	293.10
3,4-dichlorophenol*	3,4-diCl	8.585, 8.630, 8.701 (20℃) [2]; 8.630 [3]; 8.62 [16]	-1226.717415	-1226.245733	295.99
3,5-dichlorophenol*	3,5-diCl	8.185, 8.179, 8.243 (20℃) [2]; 8.18 [3] 8.25 [16]	-1226.721800	-1226.252477	294.50
3,4-dimethylphenol	3,4-diCH_3	10.32, 10.26 (22℃) [1]; 10.36, 1.356, 10.422 (20℃), 10.43 (20℃) [2]; 10.32 [19]	-386.067006	-385.584740	302.63
3,5-dimethylphenol	3,5-diCH_3	10.15, 10.02, 10.13 (19℃), 10.0 (28℃), 10.25 (18℃) [1]; 10.19, 10.203, 10.23 (20℃), 10.270 (20℃) [2]; 10.17 [19]	-386.069217	-385.587427	302.33
4-chloro-3,5-dimethylphenol	3,5-diCH_3, 4-Cl	9.702, 9.71 (20℃), 9.778 (20℃) [2]	-845.700342	-845.221604	300.41
3-fluorophenol*	3-F	9.28 [1,19] 9.29, 9.21, 8.81 [2]; 9.29 [13]	-406.707012	-406.232151	297.98
4-fluorophenol	4-F	9.81, 9.96 [1]; 9.91, 9.89, 9.75, 9.46 [2]; 9.89 [13]; 9.95 [19]	-406.705324	-406.227079	300.10
3-methylphenol	3-CH_3	10.08, 10.091, 10.00, 10.01 (22℃) [1]; 10.098, 10.09, 9.82, 10.165(20℃) [2]; 10.09 [13]; 10.08 [19]	-346.762954	-346.282514	301.48
4-methylphenol	4-CH_3	10.262, 10.19, 10.25, 10.22, 10.14 (23℃) [1]; 10.276, 10.26, 10.27, 10.10, 10.02, 10.30 (20℃), 10.349 (20℃) [2]; 10.26 [13]; 10.19 [19]; 10.08 [21]	-346.762173	-346.281020	301.93
3-methoxyphenol*	3-OCH_3	9.649, 9.65 [1]; 9.652, 9.65, 9.63, 9.62 (H_2O) [2]; 9.65[13,19]	-421.973798	-421.494494	300.77
4-methoxyphenol	4-OCH_3	10.209, 10.20 [1]; 10.21, 10.24 (H_2O), 10.12, 10.13 (10℃), 9.89 (30℃), 10.05 [2]; 10.21 [13]; 10.20 [19]; 10.21 [21]	-421.970978	-421.488609	302.69
3-methylsulfonylphenol	3-SO_2CH_3	9.33 [1,19]; 8.75, 8.79 [2]	-895.388738	-894.917387	295.78
4-methylsulfonylphenol*	4-SO_2CH_3	7.83 [1,19]; 8.28, 8.43 [2]	-895.390915	-894.922239	294.10
3-nitrophenol*	3-NO_2	8.393, 8.38, 7.15, 8.346 [1]; 8.35, 8.12, 8.04, 8.23, 8.18, 8.360, 8.421 (20℃) [2]; 8.36 [13]; 8.35 [19]; 8.33 [27]	-511.989125	-511.519085	294.95
4-nitrophenol	4-NO_2	7.149, 6.99, 7.16, 7.14, 7.15, 7.185 [1]; 7.156, 7.14, 7.151, 7.16, 6.98, 7.02, 6.89, 6.96, 7.14 (H_2O)[2]; 7.15 [13]; 7.05 [17]; 7.14 [19]; 7.06 [21]; 7.17 [27]	-511.993591	-511.533802	288.52
dichloroxylenol	2,3-diCl; 5,6-diMe	8.28 [2]	-1305.326937	-1304.853931	296.82
4-hydroxybenzothiazole		8.85 [1]	-797.941558	-797.467081	297.74
4-hydroxyisoquinoline*	4-OH	8.70 [4]	-477.125793	-476.654574	295.69
5-hydroxyisoquinoline*	5-OH	8.47 [4]	-477.126500	-476.654146	296.41
6-hydroxyisoquinoline	6-OH	9.17 [4]	-477.129243	-476.658218	295.57
7-hydroxyisoquinoline*	7-OH	8.90 [4]	-477.127897	-476.654781	296.89
8-hydroxyisoquinoline	8-OH	8.42 [4]	-477.126589	-476.655751	295.46

TABLE S3 (cont.)

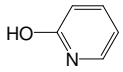
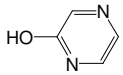
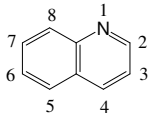
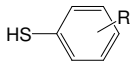
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
2-hydroxypyridine*		11.65 (20℃), 11.99 [4]; 11.99 [12]	-323.527740	-323.040848	305.53
2-hydroxypyrazine		8.25 (20℃) [4]; 7.28 [12]	-339.555783	-339.089857	292.37
					
3-hydroxyquinoline*	3-OH	8.08 (20℃), 8.09 (20℃) [4]	-477.128372	-476.656932	295.83
5-hydroxyquinoline*	5-OH	8.56 (20℃) [4]	-477.127957	-476.655497	296.47
6-hydroxyquinoline*	6-OH	8.90 (20° C)[4]	-477.129404	-476.655488	297.39
7-hydroxyquinoline*	7-OH	8.87 (20℃) [4]	-477.130547	-476.657029	297.14
8-hydroxyquinoline*	8-OH	9.812, 9.814, 9.91 (20℃), 9.82 (20℃), 9.89 (20±1℃), 9.7 (18℃), [4]; 10.369, 10.377, 9.71, 9.813 [12]	-477.131286	-476.652000	300.76
4-amino-8-hydroxyquinoline*	4-NH_2, 8-OH	10.71 (20° C)[4]	-532.500780	-532.017900	303.01
5-amino-8-hydroxyquinoline*	5-NH_2, 8-OH	11.24 (20℃) [4]	-532.488826	-532.001432	305.84
8-hydroxy-2-methylquinoline	2-CH_3, 8-OH	10.161, 10.31 [4]	-516.440717	-515.960088	301.60
8-hydroxy-4-methylquinoline	4-CH_3, 8-OH	9.99 [4]	-516.438145	-515.957628	301.53
thiols					
					
thiophenol=benzenethiol	H	6.615, 6.62 (23℃), 6.43 (35℃) [2]; 6.62 [13]	-630.437478	-629.971459	292.43
2-methyl benzenethiol*	2-CH_3	6.64 [2]	-669.742849	-669.274288	294.03
3-methyl benzenethiol*	3-CH_3	6.660, 6.58 [2]	-669.744043	-669.277215	292.94
4-methyl benzenethiol*	4-CH_3	6.820, 6.50(35℃), 6.52(23℃)[2]	-669.743726	-669.276622	293.11
3-methoxybenzenethiol*	3-OMe	6.385 [2]	-744.954590	-744.488500	292.48
3-chlorobenzenethiol*	3-Cl	5.780 [2]	-1090.070722	-1089.608065	290.32
4-bromobenzenethiol*	4-Br	6.020 [2]	-3204.686713	-3204.223250	290.83
3-nitrobenzenethiol*	3-NO_2	5.241 [2]	-834.969095	-834.509520	288.39
4-methoxybenzenethiol*	4-OMe	6.775 [2]	-744.953515	-744.485872	293.45
4-chlorobenzenethiol*	4-Cl	6.135, 5.9 (23℃) [2]	-1090.070706	-1089.606959	291.01
4-nitrobenzenethiol*	4-NO_2	4.715 [2]	-834.972885	-834.520094	284.13
4-acetylbenzenthiol	4-COMe	5.33 [9]; 5.0 [10]	-783.084277	-782.624757	288.35
	R-SH				
butane-1-thiol*	n-C_4H_9	10.66 (20℃) [6]	-556.631210	-556.150632	301.57
2-methylbutane-2-thiol*	$C(CH_3)_2CH_2CH_3$	11.22 [3]	-595.929177	-595.446254	303.04
ethanethiol	CH_2CH_3	10.61, 10.50 (20℃) [2]; 10.60 (20℃) [6]	-478.025170	-477.545098	301.25
2-ethoxyethanethiol*	$CH_2CH_2OCH_2CH_3$	9.38 [2, 3]	-631.842033	-631.364826	299.45
methyl thioglycollate	CH_2COOCH_3	8.08 [2]	-666.594983	-666.124256	295.39
ethyl-2-mercaptoacetate*	$CH_2COOCH_2CH_3$	7.95 [3]	-705.901079	-705.432246	294.20
2-mercaptoethanol	CH_2CH_2OH	9.72, 9.44, 9.48 (20℃), 9.32 (30℃), 9.43 [2]	-553.248120	-552.771022	299.38
methanethiol	CH_3	10.33 [2, 13]	-438.720141	-438.241225	300.52
phenyl-methanethiol*	$CH_2C_6H_5$	9.43 [2, 13]	-669.741602	-669.263979	299.71
2-mercapto-2-methyl-1-propanol	$C(CH_3)_2CH_2OH$	9.85 [2]	-631.849753	-631.368094	302.25
3-mercaptopropane-1,2-diol	$CH_2CH(OH)CH_2OH$	9.46, 9.51 [2]	-667.771841	-667.296639	298.19
prop-2-ene-1-thiol*	$CH_2CH=CH_2$	9.96 [2]	-516.101548	-515.625701	298.60
2-methylpropane-2-thiol	$C(Me)_3$	11.22, 11.00 [2]	-556.630535	-556.147960	302.82
2-propanethiol*	CH(Me)2	10.86 [2]	-517.328662	-516.847683	301.82
2,3-dimercapto-1-propanol* (pKa1)	$CH_2CH(SH)CH_2OH$	8.62 [2]	-990.762978	-990.293383	294.68

TABLE S3 (cont.)

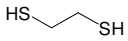
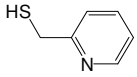
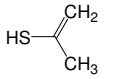
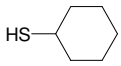
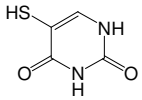
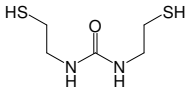
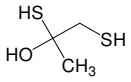
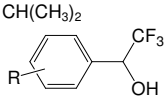
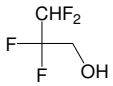
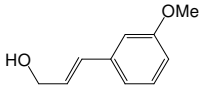
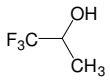
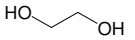
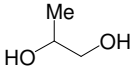
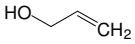
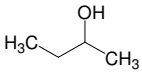
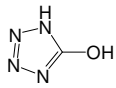
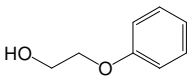
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
2,3-dimercapto-1-propanol (pKa2)	$CH_2CH(SH)CH_2OH$	10.57 [2]	-990.293383	-989.810787	302.83
thioglycollic acid*	CH_2COOH	10.40 [2, 13]	-666.152199	-665.669688	302.78
2,2,2-trifluoroethane thiol*	CH_2CF_3	7.30 [25]	-775.789877	-775.321418	293.96
3-thiopropionic acid*	CH_2CH_2COOH	10.05 (30℃) [22]; 10.6 [23]; 10.27 (20℃) [24]	-666.152407	-665.669739	302.88
3-mercaptopropan-1-ol*	$(CH_2)_3OH$	10.19 [8]	-592.551770	-592.072586	300.69
methyl 3-mercaptopropanoate*	CH_2CH_2COOMe	9.33 [25]	-705.902180	-705.424705	299.62
1,2-ethanedithiol		9.05, 8.96 (30℃) [2]	-876.240067	-875.763672	298.94
1,2-ethanedithiol		10.56, 10.54 (30℃) [2]	-875.763672	-875.279361	303.91
2-pyridyl-methanethiol		8.82 [2]	-685.791029	-685.315047	298.68
prop-1-ene-2-thiol		7.86 [13]	-516.107257	-515.637983	294.47
cyclohexanethiol		10.69 [5]	-634.036391	-633.555130	302.00
5-mercaptouracil		5.30 [2]	-813.061837	-812.600320	289.61
butane-1,4-dithiol*	$HS\text{-}(CH_2)_4\text{-}SH$	9.98 (30℃) [7]	-954.845371	-954.366727	300.35
1,3-bis(2-mercaptoethyl)urea*		9.26 (30℃) [7]	-1178.920426	-1178.443513	299.27
2,3-dimercaptopropan-2-ol*		9.04 (30℃) [7]	-990.767440	-990.294510	296.77
alcohols					
	$R\text{-}CH_2OH$				
1-butanol	$n\text{-}C_3H_7$	16.10 [2]	-233.640243	-233.130552	319.84
ethanol	CH_3	15.93, 15.9, 16.0 [2], 15.5 [13]	-155.034747	-154.525595	319.50
2-methoxyethanol	CH_2OCH_3	14.20 [2]	-269.542793	-269.037336	317.18
2,2-dichloroethanol	$CHCl_2CH_2OH$	12.89 [2]	-1074.296785	-1073.799523	312.04
2,2,2-trichloroenthanol	$C(Cl)_3$	12.25,12.24 [2]; 12.24 [13]	-1533.914970	-1533.424950	307.49
2,2,2-trifluoroethanol	CF_3	12.37(H_2O), 12.39, 12.8, 12.5 [2]	-452.799499	-452.308251	308.26
2,2,2-trinitroethanol	$C(NO_2)_3$	12.367 [1]; 12.37 [2, 3,13]	-768.563479	-768.116775	280.31
methanol	H	15.5, 15.09 [2]; 15.5 [13]	-115.726547	-115.219074	318.44
phenyl-methanol	C_6H_5	15.40 [2]	-346.748604	-346.243018	317.26
1-propanol	C_2H_5	16.10 [2]	-194.337434	-193.827948	319.71
2-methyl-propan-1-ol	$CH(CH_3)_2$	16.10 [15]	-233.639693	-233.126314	322.15
					
2,2,2-trifluoro-1-phenyl-ethanol	H	11.90 [2]	-683.814142	-683.323923	307.62
2,2,2-trifluoro-1-(4-tollyl)-ethanol	4-Me	12.04 [2]	-723.121073	-722.629909	308.21
2,2,2-trifluoro-1-(4-methoxyphenyl)-ethanol	4-OMe	12.24 [2]	-798.332141	-797.840626	308.43
2,2,2-trifluoro-1-(3-nitrophenyl)-ethanol	3-NO_2	11.23 [2]	-888.345247	-887.859396	304.88
2,2,3,3-tetrafluoro-1-propanol		12.74 [2]	-591.336578	-590.844603	308.72
3-(4-hydro-3-methoxyphenyl)-2-propen-1-ol		9.54 [2]	-613.891910	-613.414946	299.30

TABLE S3 (cont.)

Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
1,1,1-trifluoropropan-2-ol		12.37 [26]	-492.104435	-491.612365	308.78
1,2-ethanediol (ethylene glycol)		15.40 [2]	-230.255795	-229.755239	314.10
1,2-propanediol		14.90 [2]	-269.563675	-269.063404	313.93
1,3-propanediol		15.10 [2]	-269.560951	-269.062616	312.71
prop-2-en-1-ol		15.50 [2]	-193.111685	-192.605620	317.56
2-methyl-2-propanol	$C(CH_3)_3$-OH	16.90 [14]	-233.647091	-233.135911	320.77
2-butanol		17.60 [2]	-233.642747	-233.127918	323.06
2-propanol	$(CH_3)_2$CH-OH	15.70 [2, 5]	-194.342158	-193.832116	320.06
1,4-butanediol	HO-$(CH_2)_4$-OH	15.10 [2]	-308.865540	-308.356939	319.15
5-hydroxytetrazole		10.26 [22]	-333.052975	-332.573352	300.97
2-phenoxyethanol		15.1 [2]	-461.268216	-460.764973	315.79

* A conformational search was carried out on these compounds using the GMMX feature of PCModel (see text for more details)

$ kcal/mol

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TABLE S4: Hydroxamic acids and oximes

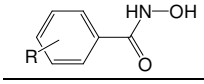
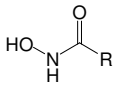
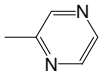
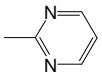
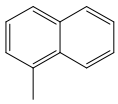
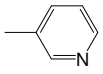
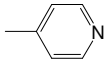
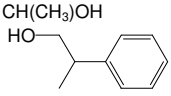
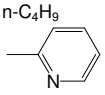
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
Hydroxamic acids					
benzohydroxamic acid*	H	8.43 (20℃); 8.805 (20℃), 8.91, 8.43 (30℃) [2] ; 8.75 [5]; 8.86, 8.9 [7]; 8.50 [10]	-476.106915	-475.634528	296.43
2-aminobenzohydroxamic acid*	2-NH_2	9.17 [1]; 9.00 (30℃) [2]	-531.470344	-530.997007	297.02
4-aminobenzohydroxamic acid*	4-NH_2	9.42, 9.32 [2]	-531.476125	-530.998108	299.96
4-chlorobenzohydroxamic acid*	4-Cl	8.58 [4]	-935.740175	-935.269446	295.39
2-chlorobenzohydroxamic acid*	2-Cl	7.85 [2]	-935.733513	-935.260785	296.64
4-cyanobenzohydroxamic acid*	4-CN	8.26, 8.16 (30.5℃) [2]	-568.357910	-567.890709	293.17
2-flurobenzohydroxamic acid*	2-F	8.00 [2]	-575.354503	-574.882255	296.34
4-flurobenzohydroxamic acid*	4-F	8.81, 8.70 (30℃) [2]	-575.357132	-574.885600	295.89
4-methoxybenzohydroxamic acid*	4-OCH_3	9.15, 8.91(30℃), 9.03 (30.5℃), 9.00 (20℃) [2]; 8.99 [6]; 9.12, 9.1 [7]; 8.76 [11]	-590.626514	-590.151928	297.81
3-nitrobenzohydroxamic acid*	3-NO_2	8.40 [2]	-680.636521	-680.169038	293.35
4-nitrobenzohydroxamic acid*	4-NO_2	8.35 (20℃), 8.12, 8.01 (30℃) [2]	-680.636697	-680.171038	292.21
salicylohydroxamic acid*	2-OH	7.46 (30℃), 7.56 (33℃), 7.43 [2]; 7.43 [4]	-551.341481	-550.876061	292.06
					
acetohydroxamic acid*	CH_3	8.70, 9.40 [2], 9.40 [6], 9.46 [4]; 9.36 [7]; 9.02 [10]; 9.31 [12]	-284.394531	-283.918514	298.72
phenylacetohydroxamic acid*	$CH_2C_6H_5$	9.18 [6]; 9.23 [4]	-515.409596	-514.936330	296.98
n-butyrohydroxamic acid*	n-C_3H_7	9.47 [6]	-362.999005	-362.521712	299.51
2-pyrazinecarbohydroxamic acid*		8.10 [2]	-508.197362	-507.728871	293.98
pyrimide-2-carbohydroxamic acid*		7.88 [2, 8]	-508.203162	-507.734551	294.06
formohydroxamic acid*	H	8.65 [2]	-245.081836	-244.609404	296.46
hexanohydroxamic acid*	n-C_5H_9	9.75, 9.48 (30℃) [2]	-441.604951	-441.127553	299.57
1-naphthohydroxamic acid*		7.70 [2]; 7.75 [4]	-629.723774	-629.249946	297.33
nicotinhydroxamic acid* (3-pyridinecarbohydroxamic acid)		7.60 (30℃), 8.30, 8.09 [2]; 8.27 [4]; 8.30 [3]; 8.09 [7]	-492.152013	-491.683062	294.29
isonicotinhydroxamic acid* (4-pyridinecarbohydroxamic acid)		7.85, 7.80 [2]; 7.94 [4]; 7.67 [7]	-492.151718	-491.684182	293.38
propanehydroxamic acid* =propionohydroxamic acid	n-C_2H_5	9.46 (20C) [2]; 9.52 [4]; 9.45 [6]; 9.36, 9.4 [7]	-323.696367	-323.218353	299.96
2-hydroxypropanehydroxamic acid*	$CH(CH_3)OH$	9.35 [2]	-398.919733	-398.442220	299.64
tropohydroxamic acid*		9.00 [2]	-629.932638	-629.457668	298.05
pentanohydroxamic acid*	n-C_4H_9	9.37 [2]	-402.301998	-401.824655	299.54
picolinhydroxamic acid* (2-pyridinecarbohydroxamic acid)		8.50, 8.7 [2]; 8.85 [4]; 8.60 [3]; 8.39 [7]	-492.158293	-491.681812	299.00
glycinehydroxamic acid* =amino acetohydroxamic acid	CH_2NH_2	9.32 [7]; 9.94 [13]	-339.742654	-339.266770	298.62

TABLE S4 (cont.)

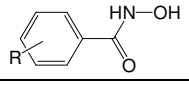
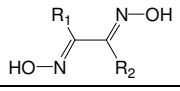
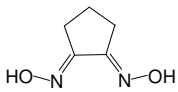
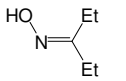
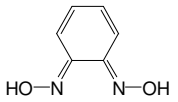
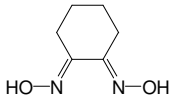
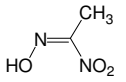
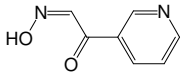
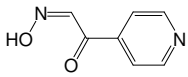
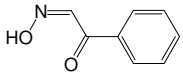
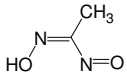
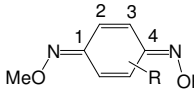
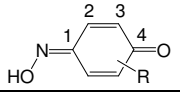
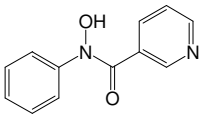
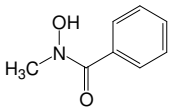
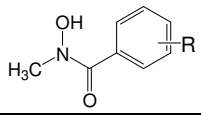
Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
					
2-nitrobenzohydroxamic acid*	2-NO_2	7.05 (20℃), 8.2 (30℃) [2]	-680.630323	-680.156105	297.58
2-methoxybenzohydroxamic acid*	2-OMe	8.90 (30℃) [2]	-590.623641	-590.147693	298.66
4-methylbenzohydroxamic acid*	4-Me	9.05, 8.93 (30.5℃), 8.93 [2]	-515.413962	-514.940913	296.84
2-methylbenzohydroxamic acid*	2-Me	8.55 (20±1℃) [2]	-515.404601	-514.930220	297.68
4-bromobenzohydroxamic acid*	4-Br	8.68 [2]	-3050.355637	-3049.885324	295.13
Oximes					
					
ethanedial dioxime	R_1, R_2=diH	8.88, 9.1, 9.05 [2]	-338.471811	-337.997990	297.33
1-chloro-ethanedial dioxime*	R_1=Cl, R_2=H	8.35, 8.13 [2]	-798.101639	-797.636552	291.85
ethanediamide dioxime* (pKa2)	R_1, R_2=di-NH_2	11.37 (20℃); 10.62 (26℃) [2]	-449.213024	-448.721237	308.60
2,3-butanedione dioxime* (pKa1)	R_1, R_2=di-CH_3	10.6, 10.42, 10.54 [2]	-417.084935	-416.601710	303.23
2,3-butanedione dioxime (pKa2)		11.9, 11.85, 12.05 [2]	-416.601710	-416.102040	313.55
1,2-cyclopentanedione dioxime* (pKa1)		10.1 [2]	-455.186720	-454.703862	303.00
3-pentanone oxime*		12.6 [2]	-327.051291	-326.556495	310.48
1,2-benzoquinone dioxime*		6.93 [2]	-492.070041	-491.606226	291.05
1,2-cyclohexanedione dioxime* (pKa1)		10.68 [2]	-494.484324	-494.001066	303.25
1,2-cyclohexanedione dioxime (pKa2)		12.16 [2]	-494.001066	-493.501260	313.63
trifluoroacetalhyde oxime*	CF_3-C=N-OH	8.90 [8]	-506.892309	-506.423380	294.26
hexafluoroaceton oxime*	$(CF_3)_2$C=N-OH	6.00 [8]	-843.941552	-843.485332	286.28
1-nitro-ethanal oxime		7.4 [2]	-413.665090	-413.204393	289.09
2-oxo-2-3-pyridylethanal oxime		7.8 [2]	-530.232086	-529.766628	292.08
2-oxo-2-4-pyridylethanal oxime		7.8 [2]	-530.230473	-529.766468	291.17
2-oxo-2-phenylethanal oxime		8.25 [2]	-514.187155	-513.719528	293.44
1-nitroso-ethanaloxime*		5.81 [2]	-338.447394	-337.993564	284.78
					
1,4-benzoquinone dioxime 1-O-methyl ester	H	9.2 [2]	-531.366167	-530.895398	295.41
2-bromo-1,4-benzoquinone dioxime 1-O-methyl ester	2-Br	8.7 [2]	-3105.610091	-3105.143790	292.61
3-bromo-1,4-benzoquinone dioxime 1-O-methyl ester	3-Br	8.6 [2]	-3105.601564	-3105.135451	292.49
2-chloro-1,4-benzoquinone dioxime 1-O-methyl ester	2-Cl	8.7 [2]	-990.994480	-990.527695	292.91
3-chloro-1,4-benzoquinone dioxime 1-O-methyl ester	3-Cl	8.6 [2]	-990.986714	-990.519957	292.89

TABLE S4 (cont.)

Compound	Structure	Experimental pK_a [ref]	$E_{neutral}$ (E_h)	E_{anion} (E_h)	$\Delta E^{\$}$
					
1,4-benzoquinone 1-oxime*	H	6.35 [2]	-436.772956	-436.316208	286.61
2-methyl-1,4-benzoquinone 1-oxime*	2-Me	6.95 [2]	-476.070426	-475.612724	287.21
3-methyl-1,4-benzoquinone 1-oxime*	3-Me	6.9 [2]	-476.081564	-475.622257	288.22
2-bromo-1,4-benzoquinone 1-oxime*	2-Br	5.7 [2]	-3011.009357	-3010.557518	283.53
3-bromo-1,4-benzoquinone 1-oxime*	3-Br	5.55 [2]	-3011.019664	-3010.567042	284.02
2-chloro-1,4-benzoquinone 1-oxime*	2-Cl	5.7 [2]	-896.394384	-895.941830	283.98
3-chloro-1,4-benzoquinone 1-oxime*	3-Cl	5.6 [2]	-896.403853	-895.950752	284.33
N-phenyl-3-pyridinecarbohydroxamic acid*		8.00 [2]	-723.152694	-722.679312	297.05
N-phenyl acetohydroxamic acid		8.10 [2]; 8.34 [10]	-515.402935	-514.918434	304.03
					
N-methylbenzohydroxamic acid	H	8.28 [9, 11]; 7.87 [10]	-515.401005	-514.919578	302.10
N-methyl-(4-cholorobenz)hydroxyomic acid	4-Cl	8.17 [9]	-975.034406	-974.553950	301.49
N-methyl-(4-methoxybenzo)hydroxyomic acid	4-OMe	8.64 [9]; 8.67 [11]	-629.919581	-629.436970	302.84
N-methyl-(4-trifluoromethylbenzo)hydroxyomic acid	4-CF3	8.06 [9]	-852.468356	-851.989472	300.50
N-methyl-(4-nitrobenzohydroxyomic acid	4-NO2	7.91 [9]; 7.94 [11]	-719.931366	-719.456927	297.72
N-methyl-(4-methylbenz)hydroxyomic acid	4-Me	8.46 [9]; 8.50 [11]	-554.708188	-554.226109	302.51
N-methyl-(3-methylbenz)hydroxyomic acid	3-Me	8.52 [9]	-554.707778	-554.225835	302.42
N-methyl-(3-methoxy-4-methylbenz)hydroxyomic acid	3-OMe	8.41 [9]	-669.223826	-668.741592	302.61
N-methyl-(3-nitro-4-chlorobenz)hydroxyomic acid	3-NO2	7.78 [9]	-1179.549852	-1179.072500	299.54
N-methyl-(3,5-dinitrobenz)hydroxyomic acid	3,5-diNO2	7.41 [9]	-924.454407	-923.978422	298.69

* A conformational search was carried out on these compounds using the GMMX feature of PCModel (see text for more details)

$ kcal/mol

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