Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Fast and Accurate Prediction of Proton Affinities: Revisiting the Extended Koopmans' Theorem for Protons

Laura Pedraza-González[a], Jorge Charry[a], William Quintero[a], Jorge Alí-Torres[a] and Andrés Reyes*[a]

[a]Departament of Chemistry, Universidad Nacional de Colombia, Av. Cra. 30 #45-03 Bogotá, Colombia.
*To whom correspondence should be addressed. E-mail: areyesv@unal.edu.co

Table S1: Structural formula, APMO/KT (PA_{KT}), APMO/KT-SC (PA_{KT}^{SC}), APMO/KT-SC-FG ($PA_{KT}^{SC\text{-}FG}$) and experimental (PA_{exp}) gas phase proton affinities for the 300 organic molecules of the test set, calculated at the DFT(B3LYP)/6-311++G(2d,2p)//APMO-KT-SC-FG/6-311G/DZSPDN level of theory.

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
	Amine				
1	NH_3	384.70	200.57	204.84	204.02
2	$CHF_2CH_2NH_2$	396.93	207.21	210.84	208.05
3	$CH_2FCH_2NH_2$	404.84	211.49	214.72	213.19
4	CH_3NH_2	403.84	210.95	214.23	214.87
5	$CH_3CH_2NH_2$	410.42	214.52	217.46	217.97
6	$CH_3(CH_2)_2NH_2$	412.68	215.75	218.56	219.36
7	$CH_3(CH_2)_3NH_2$	413.88	216.40	219.15	220.24
8	$(CH_3)_2CHNH_2$	416.57	217.86	220.47	220.79
9	$(CH_3)_2CHCH_2NH_2$	415.57	217.32	219.98	221.03
10	$CH_3(CH_2)_9NH_2$	415.32	217.18	219.86	222.40
11	$(CH_3)_2CHN(CH_3)_2$	441.17	231.20	232.53	231.98
12	$CH_3(CH_2)_8NH_2$	415.26	217.15	219.82	222.28
13	$(c\text{-}C_6H_{11})CH_2NH_2$	419.84	219.63	222.07	221.50
14	$(n\text{-}C_4H_9)_3N$	454.48	238.42	239.05	238.65
15	$(sec\text{-}C_4H_9)_2NH$	443.87	232.67	233.85	234.39
16	$(c\text{-}C_6H_{11})CH_2N(CH_3)_2$	444.56	233.04	234.19	233.17
17	$(CH_3)_2CHCH_2N(CH_3)_2$	439.54	230.32	231.73	231.52
18	$CH_3CH_2(CH_3)CHNH_2$	419.52	219.46	221.92	222.20
19	$(sec\text{-}C_4H_9)(CH_3)_2N$	443.43	232.43	233.64	233.25
20	$(t\text{-}C_4H_9)(CH_3)_2N$	446.38	234.03	235.08	234.13
21	$(t\text{-}C_5H_{11})(CH_3)_2N$	448.77	235.32	236.25	234.82
22	$H_2N(CH_2)_2CN$	395.80	206.59	210.29	207.07
23	$(CH_3)_2NCN$	388.08	202.40	206.50	203.66
24	$(CH_3)_3CNH_2$	422.35	220.99	223.30	223.26
25	$CH_3CH_2NHCH_3$	424.61	222.22	224.41	225.19
26	$(CH_3)_3N$	429.80	225.03	226.95	226.79
27	$(CH_3)_2CHNHCH_3$	429.94	225.11	227.02	227.61
28	$(CH_3CH_2)_2NH$	430.13	225.21	227.11	227.63
29	$CH_3CH_2N(CH_3)_2$	436.03	228.41	230.01	229.50
30	$(CH_3)_2NH$	418.64	218.98	221.49	222.16
31	$CH_3(CH_2)_4NH_2$	414.50	216.74	219.46	220.72
32	$CH_3(CH_2)_5NH_2$	415.01	217.01	219.70	221.68
33	$CH_3(CH_2)_6NH_2$	415.07	217.04	219.73	221.56
34	$CH_3(CH_2)_7NH_2$	415.19	217.11	219.79	222.01
35	$(C_3H_7)_3N$	450.72	236.38	237.21	236.90
36	$(C_2H_5)_2NCH_3$	441.30	231.27	232.59	232.10
37	$(CH_3)_2N(n\text{-}C_3H_7)$	437.97	229.47	230.96	230.10
38	$CH_3CH_2C(CH_3)_2NH_2$	424.98	222.42	224.59	224.14
39	$CH(CH_3)_2NHCH_2CH_3$	435.02	227.87	229.51	229.45
40	$(C_3H_7)_2NH$	434.08	227.36	229.05	230.00
41	$(C_4H_7)N(CH_3)_2$	439.04	230.05	231.48	231.64

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
42	$(C_2H_5)_2N(C_3H_7)$	448.77	235.32	236.25	233.94
43	$(C_4H_9)_2NH$	436.15	228.48	230.07	231.48
44	$CH_2(CH_3)CH_2NH_2$	415.19	217.11	219.79	219.30
45	$(C_6H_{11})NH_2$	421.41	220.48	222.84	223.33
46	$(C_2H_5)_3N$	446.00	233.82	234.90	234.66
47	$(c\text{-}C_3H_5)NH_2$	408.67	213.57	216.59	216.20
48	$(c\text{-}C_6H_{11})N(CH_3)_2$	445.63	233.62	234.71	235.09
49	$(t\text{-}C_4H_9)_2NH$	450.27	236.14	236.99	236.11
	Aniline				
50	Aniline	410.29	214.45	211.68	210.92
51	p-Chloroaniline	404.83	211.49	209.09	208.84
52	m-Chloroaniline	404.58	211.36	208.97	207.48
53	p-Fluoroaniline	404.33	211.22	208.85	208.29
54	m-Fluoroaniline	403.58	210.81	208.49	207.29
55	p-Hydroxyaniline	419.64	219.53	216.12	214.82
56	p-Aminoaniline	419.02	219.18	215.82	216.52
57	m-Trifluromethylaniline	402.01	209.96	207.75	204.80
58	o-Methylaniline	413.49	216.19	213.20	212.93
59	m-Methylaniline	412.99	215.92	212.96	214.10
60	N-Methyl-aniline	425.04	222.45	218.68	219.07
61	p-Methylaniline	413.24	216.05	213.08	214.32
62	o-Methoxyaniline	424.10	221.94	218.24	216.35
63	p-Methoxyaniline	413.56	216.22	213.23	215.18
64	m-(Methylthio)aniline	410.48	214.56	211.77	215.61
65	2,6-Dimethylaniline	418.08	218.67	215.37	215.51
66	p-Chloro-N,N-dimethylaniline	431.19	225.79	221.60	220.58
67	p-Fluoro-N,N-dimethylaniline	430.75	225.55	221.39	221.03
68	N,N-Dimethylaniline	436.34	228.58	224.05	224.93
69	m-Ethylaniline	414.06	216.50	213.47	214.60
70	N-Ethylaniline	430.25	225.28	221.16	221.03
71	o-Methyl-N,N-dimethylaniline	438.97	230.01	225.30	227.49
72	p-Nitroaniline	396.11	206.76	204.94	206.98
73	p-Nitro-N,N-dimethylaniline	423.10	221.40	217.76	214.32
74	p-Nitro-N,N,2,6-tetramethylaniline	429.06	224.63	220.59	219.50
75	p-Nitro-N-methylaniline	411.17	214.93	212.10	213.10
	Ester				
76	$HCOO(n\text{-}C_3H_7)$	367.31	191.14	192.03	192.38
77	$HCOO(n\text{-}C_4H_9)$	368.32	191.68	192.69	192.64
78	$HCOOCH(CH_3)_2$	372.90	194.17	195.70	193.91
79	$CH_3COO_2CH_3$	372.40	193.90	195.37	196.37
80	$C_2H_5COOCH_3$	376.60	196.18	198.13	198.42
81	$CH_3COOCH_2CH_3$	377.86	196.86	198.95	199.74
82	$C_3H_7COOCH_3$	378.86	197.40	199.61	199.90
83	$i\text{-}C_3H_7COOCH_3$	380.30	198.19	200.56	199.95
84	$C_3H_7COOCH_3$	379.30	197.64	199.90	199.95
85	$t\text{-}C_4H_9COOCH_3$	383.32	199.82	202.54	202.01
86	$HCOOCH_3$	358.97	186.61	186.56	187.02
87	$(c\text{-}C_3H_5)COOCH_3$	381.06	198.59	201.05	201.29

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
88	$CH_3CHCHCOOCH_3$	384.88	200.67	203.56	203.49
89	CH3COOCN	346.89	180.06	178.63	178.23
	Alcohol				
90	CH_2FCH_2OH	341.90	177.35	176.58	171.03
91	CHF_2CH_2OH	340.39	176.54	175.79	173.85
92	CH_3OH	346.42	179.81	178.98	180.28
93	CH_3CH_2OH	359.47	186.89	185.90	185.56
94	$CH_3(CH_2)_2OH$	362.42	188.49	187.46	187.98
95	$CH_3(CH_2)_3OH$	364.43	189.57	188.52	188.62
96	i-$CH_3(CH_2)_2OH$	372.46	193.93	192.78	189.77
97	$(CH_3)_2CH_2OH$	364.99	189.88	188.82	189.70
98	$(CH_3)_3CCH_2OH$	368.07	191.55	190.45	190.13
99	H_2O	315.16	162.85	162.41	165.15
100	$CH_3CH_2CH(OH)CH_3$	375.97	195.84	194.64	194.79
101	$CH_3(CH_2)_4OH$	365.56	190.19	189.12	190.01
102	$CH_3(CH_2)_5OH$	366.06	190.46	189.39	190.97
103	$CH_3(CH_2)_6OH$	366.31	190.60	189.52	190.97
104	$CH_3(CH_2)_7OH$	366.50	190.70	189.62	190.97
105	(c-C_5H_9)OH	369.82	192.50	191.38	191.00
106	(c-C_6H_{11})CH_2OH	369.51	192.33	191.22	191.71
	Amide				
107	$(CH_3)_2NCHO$	389.65	203.26	210.19	212.12
108	CH_3CONH_2	382.19	199.21	205.60	206.41
109	$CH_3CH_2CONH_2$	385.76	201.15	207.80	209.42
110	n-C_3H_7NHCHO	386.14	201.35	208.03	209.94
111	$CH_3CONHCH_2$	391.29	204.14	211.19	212.36
112	$CH_3CONHC_2H_5$	395.18	206.25	213.58	214.63
113	$CH_3CON(CH_3)_2$	400.45	209.11	216.81	217.02
114	$CH_3CH_2CH_2CON(CH_3)_2$	403.52	210.78	218.70	220.29
115	$HCONH_2$	369.07	192.09	197.55	196.50
116	$(CH_3)_2CHCNH_2O$	388.65	202.71	209.57	209.99
117	$(CH_3)_3CONH_2$	392.29	204.69	211.80	212.50
118	$HCONHCH_3$	379.93	197.98	204.22	203.47
119	$(CH_3)_3CCON(CH_3)_2$	407.41	212.89	221.09	221.58
120	$(CH_3)_3CCH_2CON(CH_3)_2$	407.91	213.16	221.40	221.73
121	$C_3H_7CON(CH_3)\_2$	405.40	211.80	219.85	220.77
122	$CH_3CON(C_2H_5)_2$	406.47	212.38	220.51	221.18
123	$CH_2CH(CH_3)CON(CH_3)_2$	405.27	211.73	219.78	217.85
124	$CH_2CHCON(CH_3)_2$	404.71	211.42	219.43	216.13
125	2-butenamide	397.12	207.31	214.77	212.02
126	$(CH_3)_2CHCONH_2$	390.03	203.46	210.42	210.40
127	$CH_2CHCONH_2$	388.58	202.68	209.53	208.10
128	2-Azetidinone	383.12	199.72	206.18	203.78
	Aldehyde				
129	CH_2O	332.49	172.25	172.97	170.39
130	CH_3CHO	355.20	184.57	183.66	183.68
131	CH_3CH_2CHO	360.29	187.33	186.05	187.86
132	n-C_3H_7CHO	362.36	188.45	187.03	189.46

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
133	n-C_4H_9CHO	363.42	189.03	187.53	190.39
134	$(CH_3)_2CHCOH$	365.06	189.91	188.30	190.56
135	$CH_3CHCHCHO$	389.84	203.36	199.97	198.57
136	CCl_3CHO	334.30	173.23	173.82	172.63
137	CF_3CHO	312.53	161.42	163.57	163.84
138	CH_2CHCHO	375.66	195.66	193.29	190.49
139	$CH_3C(CH_3)CHO$	379.04	197.50	194.89	193.28
	Benzaldehyde				
140	Benzaldehyde	394.10	205.67	198.95	199.33
141	p-Methylbenzaldehyde	401.95	209.93	203.46	203.59
142	m-Fluorobenzaldehyde	385.82	201.18	194.18	194.62
143	m-Chlorobenzaldehyde	387.45	202.06	195.12	194.31
144	p-Trifluoromethylbenzaldehyde	381.99	199.10	191.97	192.54
145	p-Cyanobenzaldehyde	384.19	200.29	193.24	190.46
146	m-Methylbenzaldehyde	397.18	207.34	200.72	200.76
147	p-Chlorobenzaldehyde	392.91	205.03	198.26	198.69
148	p-Fluorobenzaldehyde	391.28	204.14	197.32	197.68
149	p-Nitrobenzaldehyde	376.41	196.07	188.76	190.00
	Ketone				
150	$(CH_3)_2CO$	371.90	193.62	195.44	194.07
151	$C_7H_7COCH_3$	386.20	201.39	202.76	201.39
152	$CH_3COC_2H_5$	375.53	195.60	197.30	197.73
153	n-$C_3H_7COCH_3$	377.42	196.62	198.26	199.02
154	$(CH_3)_2CHCOCH_3$	380.68	198.39	199.93	199.88
155	$(C_2H_5)_2CO$	380.18	198.12	199.68	200.00
156	$CH_3CH_2CH_2COCH_2CH_3$	384.01	200.19	201.63	201.53
157	$(C_3H_7)_2CO$	384.32	200.36	201.79	201.96
158	$(CH_3)_3COCH_3$	385.01	200.74	202.15	200.79
159	(c-$C_6H_{10}O$)	383.06	199.68	201.15	203.60
160	p-$CH_3C_6H_9O$	384.07	200.23	201.67	201.94
161	(c-C_4H_6O)	369.39	192.26	194.16	194.60
162	(c-C_5H_8O)	376.54	196.14	197.81	196.87
163	(c-$C_8H_{14}O$)	387.96	202.34	203.66	203.01
164	(c-$C_7H_{12}O$)	385.45	200.98	202.37	204.50
165	(i-$C_3H_7)_2CO$	389.47	203.16	204.43	203.23
166	(t-$C_4H_9)_2CO$	394.92	206.12	207.22	205.86
167	(c-C_3H_5)$COCH_3$	387.14	201.90	203.24	204.33
168	$(CH_3)_2SO$	401.82	209.86	210.75	211.38
169	CFH_2COCFH_2	341.39	177.08	179.84	182.31
170	CH_3COCN	344.22	178.61	181.29	178.51
	Ether				
171	CH_3OCH_3	366.56	190.73	188.69	189.29
172	$CH_3CH_2OCH_3$	375.97	195.84	193.76	193.26
173	n-$C_3H_7OCH_3$	378.36	197.13	195.05	194.77
174	$(CH_3)_2CHOCH_3$	385.70	201.11	199.01	197.49
175	$(C_2H_5)_2O$	384.01	200.19	198.09	197.99
176	$(C_3H_7)_2O$	388.34	202.54	200.43	200.26
177	$(C_4H_9)_2O$	390.91	203.94	201.81	203.63

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
178	$(C_4H_9)OCH_3$	379.99	198.02	195.93	196.06
179	$(CH_3)_2CHOCH_2CH_3$	392.35	204.72	202.59	201.41
180	$(c\text{-}C_6H_{11})_3O$	391.29	204.14	202.02	200.88
181	$(n\text{-}C_5H_{11})_2O$	392.23	204.65	202.52	203.80
182	$(c\text{-}C_6H_{11})CH_2OCH_3$	383.88	200.13	198.03	199.21
183	CH_3OCH_2CN	352.88	183.31	181.32	181.19
	Carboxylic				
184	HCOOH	343.47	178.21	179.76	177.34
185	CH_3COOH	359.60	186.95	187.80	187.31
186	C_2H_5COOH	372.40	193.90	194.18	190.54
187	CH_2FCOOH	345.35	179.23	180.69	182.93
188	$(CH_3)_2CCHCOOH$	381.50	198.83	198.71	196.70
189	$(CH_3)_2CCOOH$	374.59	195.09	195.27	195.20
190	$CH_3(CH)_2COOH$	374.34	194.95	195.15	196.89
191	$(c\text{-}C_4H_7)COOH$	371.77	193.56	193.86	195.41
192	$(c\text{-}C_6H_{11})COOH$	372.33	193.86	194.15	196.89
193	$(c\text{-}C_5H_9)COOH$	374.15	194.85	195.05	195.41
	Pyridine				
194	Pyridine	423.85	221.81	221.32	222.28
195	m-Methylpyridine	428.12	224.12	224.18	224.82
196	p-Methylpyridine	430.69	225.52	225.91	226.39
197	m-Ethylpyridine	430.37	225.35	225.70	226.43
198	o-Methylpyridine	431.38	225.89	226.37	226.84
199	p-Ethylpyridine	432.26	226.37	226.96	227.32
200	o-Ethylpyridine	433.89	227.25	228.05	227.63
201	3,5-Dimethylpyridine	432.13	226.30	226.88	228.35
202	o-Propylpyridine	435.02	227.86	228.81	228.42
203	p-Isopropylpyridine	433.64	227.12	227.89	228.42
204	o-(methylthyl)-pyridine	436.65	228.75	229.90	228.59
205	3,4-Dimethylpyridine	434.33	227.49	228.35	228.80
206	2,5-Dimethylpyridine	435.52	228.14	229.15	229.16
207	2,3-Dimethylpyridine	435.08	227.90	228.85	229.18
208	2,4-Dimethylpyridine	437.65	229.29	230.58	230.14
209	2,6-Dimethylpyridine	438.22	229.60	230.96	230.16
210	2,6-Diethylpyridine	443.18	232.29	234.28	232.39
211	Pentafluoropyridine	368.38	191.72	184.13	182.82
212	o-Chloropyridine	416.32	217.72	216.27	215.32
213	p-Chloropyridine	419.52	219.46	218.42	218.95
214	m-Chloropyridine	416.13	217.62	216.15	215.92
215	m-Fluoropyridine	413.06	215.95	214.09	215.58
216	o-Fluoropyridine	409.16	213.84	211.48	211.42
217	p-Fluoropyridine	416.63	217.89	216.48	218.24
218	m-Pyridinol	422.66	221.16	220.52	222.16
219	o-Aminopyridine	435.02	227.86	228.81	226.39
220	m-Aminopyridine	430.56	225.45	225.82	228.11
221	p-Aminopyridine	442.29	231.81	233.69	234.15
222	2,3-Cyclobutenopyridine	431.19	225.79	226.24	227.99
223	3,4-Cyclobutenopyridine	433.70	227.15	227.93	228.85

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
224	p-(t-butyl)pyridine	435.08	227.90	228.85	228.90
225	p-Ethenylpyridine	434.64	227.66	228.56	225.65
226	1,4,4-Trimethyl-1,2,3,4-tetrahydropyridine	441.42	231.34	233.10	234.20
227	1H-Pyrrolo[2,3-b]pyridine	431.75	226.09	226.62	224.71
228	m-(Trifluoromethyl)pyridine	410.98	214.83	212.70	213.31
229	o-(t-Butyl)pyridine	438.91	229.97	231.42	229.85
230	2-Chloro-6-methylpyridine	423.60	221.67	221.15	216.99
231	2-Chloro-4-methylpyridine	423.03	221.36	220.78	220.20
232	o-Pyridinecarbonitrile	409.92	214.25	211.98	208.63
233	p-Pyridinecarbonitrile	412.37	215.58	213.62	210.47
234	o-(Methylthio)pyridine	436.65	228.75	229.90	224.14
235	p-Pyridinecarboxaldehyde	417.76	218.50	217.24	216.20
236	2-chloro-6-methoxypyridine	416.00	217.55	216.06	217.47
237	o-Methoxypyridine	423.79	221.77	221.28	223.40
238	p-Trifluoromethylpyridine	410.48	214.56	212.36	213.65
239	p-Methoxycarbonylpyridine	417.13	218.16	216.82	221.46
240	o-Trifluoromethylpyridine	408.60	213.53	211.10	212.02
241	m-Pyridinecarbonitrile	410.17	214.39	212.15	209.61
242	2-Chloro-4-methylpyridine	423.03	221.36	220.78	220.17
243	p-Methoxypyridine	434.83	227.76	228.68	229.85
244	m-Methoxypyridine	425.98	222.96	222.75	225.31
245	m-(Methylthio)pyridine	426.36	223.17	223.01	223.83
246	p-(Methylthio)pyridine	434.64	227.66	228.56	228.30
247	m-Acetylpyridine	420.15	219.80	218.84	218.98
248	2,3-Cyclopentenopyridine	435.08	227.90	228.85	228.85
249	3,4-Cyclopentenopyridine	435.71	228.24	229.27	230.02
250	4-Nitropyridine	404.65	211.39	208.45	208.96
251	N,N-Dimethyl-3-pyridinamine	435.33	228.03	229.02	231.74
	Pyrazole				
252	Pyrazole	411.74	215.24	211.64	213.70
253	3(5)-Methylpyrazole	420.33	219.90	217.21	216.54
254	3(5)-(t-butyl)pyrazole	426.23	223.10	221.04	220.55
255	4-Methylpyrazole	416.69	217.93	214.85	216.73
256	4-(1)-Adamantylpyrazole	423.66	221.70	219.37	218.24
257	3,5-Dimethylpyrazole	428.18	224.15	222.30	223.11
258	3,4-Dimethylpyrazole	424.29	222.04	219.77	221.63
259	3,4,5-Trimethylpyrazole	431.82	226.13	224.66	226.89
260	1-(n-butyl)pyrazole	424.85	222.35	220.14	221.99
261	1-Adamantylpyrazole	434.14	227.39	226.16	228.13
262	3,5-Diethyl-4-methylpyrazole	435.58	228.17	227.10	227.72
263	3,5-Di(t-butyl)pyrazole	439.16	230.11	229.41	227.70
264	3-Methyl-5-tertbutylpyrazole	433.70	227.15	225.88	226.15
265	3,5-Ditertbutyl-4-methylpyrazole	442.17	231.74	231.37	231.24
266	3-Nitropyrazole	389.59	203.22	197.29	196.18
267	4-Nitropyrazole	390.03	203.46	197.57	196.51
268	3,5-Dinitropyrazole	369.13	192.12	184.03	181.50
269	p-Fluoropyrazole	400.88	209.35	204.61	206.26
270	p-Chloropyrazole	404.08	211.08	206.68	207.58

Continued on next page

	Molecule	PA_{KT}	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{exp}
271	m-Phenylpyrazole	427.49	223.78	221.85	218.50
272	p-Phenylpyrazole	418.83	219.08	216.24	216.54
273	p-CO_2Et-pyrazole	409.86	214.22	210.42	210.49
274	m-Aminopyrazole	431.13	225.75	224.21	220.24
275	p-Aminopyrazole	418.14	218.71	215.79	216.92
276	1-Methylpyrazole	419.20	219.29	216.48	217.97
277	1,3-Dimethylpyrazole	427.36	223.71	221.77	223.21
278	1,5-Dimethylpyrazole	426.48	223.24	221.20	223.30
279	1,4-Dimethylpyrazole	424.16	221.98	219.69	221.89
280	1,3,5-Trimethylpyrazole	434.14	227.39	226.16	226.89
281	1-Methyl-3-t-butylpyrazole	433.45	227.01	225.71	225.72
282	1-Methyl-5-t-butylpyrazole	431.06	225.72	224.17	224.47
283	1-Methyl-3,5-dinitropyrazole	377.35	196.58	189.35	188.53
284	1-Methyl-3-nitropyrazole	397.93	207.75	202.69	203.23
285	1-Methyl-5-nitropyrazole	397.30	207.41	202.29	202.58
286	1-Methyl-3-phenylpyrazole	434.26	227.46	226.24	222.90
287	1,5-Dimethyl-3-phenylpyrazole	440.79	231.00	230.47	228.08
288	1-Methyl-3-aminopyrazole	433.70	227.15	225.88	224.04
289	1-Methyl-5-aminopyrazole	438.72	229.87	229.13	226.94
	Sulfoether				
290	Thietane	406.66	210.48	200.71	199.52
291	Diethyl sulfide	415.51	215.28	204.41	204.76
292	Methyl ethyl sulfide	408.98	210.74	201.68	202.32
293	Tetrahydrothiophene	413.12	212.99	203.41	202.94
294	Dipropylsulfide	419.71	217.56	206.17	206.67
295	c-$C_6H_{11}SCH_3$	421.03	218.28	206.72	206.62
296	n-$(C_4H_9)_2S$	421.91	218.75	207.09	208.37
297	$CF_3CH_2SC_2H_5$	394.80	203.05	191.53	190.63
298	Dimethyl sulfide	401.95	207.93	198.74	198.59
299	Di-(methylethyl)sulfide	427.74	219.92	209.53	209.46
300	Di-(t-butyl) sulfide	439.35	225.21	214.39	213.62

Table S2: Mean absolute error (MAE), mean absolute deviation (MAD) and maximum absolute deviation (AD_{max}) for calculated APMO/KT proton affinities (PA_{KT}s) of 300 organic molecules, optimized with the HF, DFT and MP2 methods, using Equation 16. Data grouped by combination of electronic/nuclear basis sets. Values in kcal mol^{-1}

APMO/KT basis set		HF geometry			DFT geometry			MP2 geometry		
Electronic	Nuclear	MAE	MAD	AD_{max}	MAE	MAD	AD_{max}	MAE	MAD	AD_{max}
1. 6-311G	7-*s*	192.37	12.12	220.90	192.45	11.65	222.85	191.87	11.79	218.27
2. 6-311G	DZSPDN	193.55	12.10	223.60	193.72	11.64	225.73	193.14	11.76	221.15
3. 6-311G(d,p)	7-*s*	207.34	9.84	244.93	207.42	9.42	245.94	206.99	9.45	242.80
4. 6-311G(d,p)	DZSPDN	205.71	9.81	243.93	206.66	9.35	245.75	206.21	9.41	242.24
5. 6-311G++(d,p)	7-*s*	207.16	9.87	245.25	207.21	9.48	246.25	206.75	9.54	245.11
6. 6-311G++(d,p)	DZSPDN	205.50	9.91	244.24	206.43	9.44	246.00	206.00	9.50	244.55
7. cc-pVDZ	7-*s*	204.84	10.07	244.24	205.18	9.55	245.50	204.75	9.57	242.24
8. cc-pVDZ	DZSPDN	203.36	10.07	243.37	204.56	9.50	245.25	204.15	9.58	241.73
9. aug-cc-pVDZ	7-*s*	208.13	9.86	246.06	208.17	9.45	247.13	207.78	9.54	243.99
10. aug-cc-pVDZ	DZSPDN	206.38	9.93	246.38	207.34	9.49	246.88	207.01	9.51	243.43

Table S3: Mean absolute error (MAE), mean absolute deviation (MAD) and maximum absolute deviation (AD_{max}) for calculated APMO/KT-SC proton affinities (PA^{SC}_{KT}s) of 300 organic molecules, optimized with the HF, DFT and MP2 methods, using the corresponding m and b data (Table 1) in Equation 17. Data are grouped by combination of electronic/nuclear basis sets.

APMO/KT-SC basis sets		HF geometry			DFT(B3LYP) geometry			MP2 geometry		
Electronic	Nuclear	MAE	MAD	AD_{max}	MAE	MAD	AD_{max}	MAE	MAD	AD_{max}
1. 6-311G	7-*s*	2.83	1.84	12.28	2.79	1.87	11.27	2.73	1.83	11.28
2. 6-311G	DZSPDN	2.80	1.75	11.56	2.72	1.81	10.62	2.62	1.78	10.61
3. 6-311G(d,p)	7-*s*	2.67	1.88	12.53	2.65	1.95	11.37	2.61	1.89	11.63
4. 6-311G(d,p)	DZSPDN	2.61	1.81	11.91	2.60	1.90	11.19	2.59	1.86	11.47
5. 6-311G++(d,p)	7-*s*	2.66	1.86	12.30	2.63	1.95	11.16	2.61	1.90	11.49
6. 6-311G++(d,p)	DZSPDN	2.58	1.79	11.80	2.58	1.89	10.98	2.56	1.85	11.24
7. cc-pVDZ	7-*s*	2.74	1.90	13.26	2.66	1.96	11.41	2.69	1.92	11.69
8. cc-pVDZ	DZSPDN	2.65	1.81	12.71	2.61	1.90	11.20	2.66	1.87	11.48
9. aug-cc-pVDZ	7-*s*	2.78	1.94	14.04	2.74	2.00	11.84	2.76	1.97	11.94
10. aug-cc-pVDZ	DZSPDN	2.71	1.85	13.80	2.70	1.95	11.51	2.71	1.92	11.56

Table S4: Correlation parameters of calculated and experimental $PA_{KT}^{SC\text{-}FG}$ grouped by functional group for each geometry optimization, using ten different combinations of electronic and nuclear basis sets. Values in kcal mol^{-1}.

Basis set		R^2	m	b	R^2	m	b	R^2	m	b	R^2	m	b	R^2	m	b
Electronic/Nuclear		6-311G			6-311G(d,p)			6-311G++(d,p)			cc-pVDZ			aug-cc-pVDZ		
Amine																
HF	DZSPDN	0.9792	0.5002	11.9538	0.9742	0.4809	16.1325	0.9748	0.4794	16.6205	0.9725	0.4810	17.2774	0.9744	0.4719	19.7817
	7-*s*	0.9743	0.4873	18.4735	0.9722	0.4764	17.6247	0.9733	0.4715	19.6635	0.9694	0.4733	20.2255	0.9718	0.4639	22.7655
DFT	DZSPDN	0.9772	0.4902	16.2662	0.9732	0.4730	19.3436	0.9743	0.4721	19.6335	0.9714	0.4722	20.7524	0.9725	0.4631	23.3958
	7-*s*	0.9750	0.4805	21.4252	0.9722	0.4706	20.2064	0.9732	0.4679	21.2883	0.9706	0.4703	21.4657	0.9720	0.4602	24.4428
MP2	DZSPDN	0.9805	0.5045	10.5000	0.9755	0.4818	15.8066	0.9740	0.4805	16.2424	0.9717	0.4834	16.2752	0.9742	0.4708	20.3074
	7-*s*	0.9774	0.4901	17.6273	0.9756	0.4812	15.8485	0.9742	0.4806	16.0236	0.9700	0.4813	17.0550	0.9735	0.4687	21.0114
Aniline																
HF	DZSPDN	0.9084	0.4786	15.1518	0.8896	0.4539	21.2703	0.8889	0.4515	22.3261	0.8858	0.4527	22.7331	0.8719	0.4452	24.5869
	7-*s*	0.9048	0.4594	24.1968	0.8875	0.4457	24.3167	0.8925	0.4454	24.4936	0.8834	0.4453	25.5133	0.8794	0.4402	26.3251
DFT	DZSPDN	0.9087	0.4749	16.8307	0.8978	0.4505	22.6294	0.8954	0.4466	24.3912	0.8970	0.4506	23.4971	0.8900	0.4440	25.0815
	7-*s*	0.9075	0.4573	25.2084	0.8891	0.4456	24.5652	0.8945	0.4433	25.6266	0.8935	0.4454	25.5939	0.8883	0.4401	26.5634
MP2	DZSPDN	0.9102	0.4824	13.7076	0.9018	0.4637	17.0813	0.9000	0.4600	18.6841	0.9043	0.4641	17.8118	0.8992	0.4589	18.8336
	7-*s*	0.9114	0.4692	20.2646	0.9002	0.4594	18.7057	0.9009	0.4533	21.4251	0.9024	0.4592	19.7604	0.8948	0.4534	20.9699
Ester																
HF	DZSPDN	0.9898	0.6688	-53.5899	0.9901	0.6249	-48.9278	0.9907	0.6190	-46.2108	0.9905	0.6430	-54.5274	0.9916	0.6526	-60.4379
	7-*s*	0.9895	0.6650	-52.1029	0.9787	0.6466	-58.0889	0.9814	0.6000	-39.9968	0.9892	0.6358	-53.0012	0.9923	0.6502	-61.0441
DFT	DZSPDN	0.9882	0.6562	-48.9967	0.9904	0.6186	-47.0157	0.9906	0.6128	-44.3154	0.9889	0.6215	-46.8740	0.9890	0.6394	-55.9524
	7-*s*	0.9880	0.6611	-50.5156	0.9902	0.6211	-48.5735	0.9907	0.6157	-46.0529	0.9894	0.6243	-48.4837	0.9875	0.6552	-62.7801
MP2	DZSPDN	0.9910	0.6583	-49.2746	0.9955	0.6187	-46.6972	0.9946	0.6127	-43.9341	0.9957	0.6222	-46.7937	0.9939	0.6166	-46.5564
	7-*s*	0.9903	0.6631	-50.8166	0.9956	0.6223	-48.7625	0.9947	0.6164	-46.0820	0.9957	0.6261	-48.9066	0.9911	0.6371	-55.3697
Alcohol																
HF	DZSPDN	0.9339	0.5601	-15.0263	0.9115	0.5433	-15.5822	0.9133	0.5357	-12.5472	0.9131	0.5473	-15.3697	0.9030	0.5270	-9.5607
	7-*s*	0.9229	0.5356	-4.7035	0.9055	0.5289	-10.8152	0.9059	0.5229	-8.3605	0.9055	0.5317	-10.0165	0.8955	0.5139	-5.3170
DFT	DZSPDN	0.9376	0.5300	-4.6224	0.9161	0.5104	-4.2965	0.9184	0.5046	-1.9655	0.9175	0.5129	-3.8549	0.9008	0.4835	5.6481
	7-*s*	0.9292	0.5112	3.5890	0.9130	0.5054	-2.5978	0.9149	0.4963	0.9939	0.9130	0.5066	-1.5738	0.9045	0.4953	1.0045
MP2	DZSPDN	0.9445	0.5762	-19.5275	0.9188	0.5530	-18.6031	0.9207	0.5448	-15.4165	0.9213	0.5589	-19.2153	0.9086	0.5370	-12.8175
	7-*s*	0.9319	0.5504	-8.7605	0.9153	0.5460	-16.2324	0.9138	0.5382	-13.1140	0.9156	0.5489	-15.6765	0.9015	0.5301	-10.4183
Amide																
HF	DZSPDN	0.9549	0.6202	-31.3836	0.9530	0.6235	-43.1394	0.9545	0.6146	-39.0260	0.9522	0.6343	-46.1567	0.9534	0.6105	-37.9060
	7-*s*	0.9497	0.6179	-30.0021	0.9527	0.6274	-46.0132	0.9538	0.6168	-41.2608	0.9523	0.6380	-48.7979	0.9580	0.6130	-40.2447
DFT	DZSPDN	0.9417	0.6138	-28.9823	0.9444	0.6233	-43.6595	0.9467	0.6145	-39.5887	0.9437	0.6321	-46.1175	0.9512	0.6096	-38.1871
	7-*s*	0.9369	0.6191	-30.4653	0.9436	0.6252	-44.9585	0.9463	0.6160	-40.7363	0.9385	0.6415	-50.2826	0.9503	0.6124	-39.8601
MP2	DZSPDN	0.9509	0.6319	-36.2320	0.9477	0.6318	-47.3583	0.9498	0.6222	-42.9474	0.9477	0.6405	-49.7471	0.9533	0.6170	-41.4626
	7-*s*	0.9448	0.6285	-34.2453	0.9462	0.6350	-49.2384	0.9369	0.6316	-47.2772	0.9468	0.6433	-51.3422	0.9515	0.6209	-43.6383
Aldehyde																
HF	DZSPDN	0.9695	0.4866	11.1826	0.9441	0.5372	-15.7993	0.9391	0.5275	-12.1753	0.9424	0.5422	-16.3338	0.9426	0.5505	-21.0825
	7-*s*	0.9469	0.4872	11.5638	0.9427	0.5399	-18.0988	0.9407	0.5346	-16.0435	0.9407	0.5451	-18.5409	0.9387	0.5524	-23.1458
DFT	DZSPDN	0.9557	0.4708	16.4314	0.9511	0.5166	-9.4659	0.9518	0.5197	-10.4753	0.9501	0.5221	-10.3753	0.9482	0.5320	-15.6068
	7-*s*	0.9542	0.4739	15.5796	0.9504	0.5184	-10.6047	0.9506	0.5202	-11.1767	0.9492	0.5234	-11.2893	0.9455	0.5342	-16.9025
MP2	DZSPDN	0.9616	0.4750	14.8084	0.9530	0.5311	-15.2559	0.9541	0.5334	-15.9993	0.9535	0.5357	-15.8945	0.9541	0.5453	-21.0665
	7-*s*	0.9610	0.4772	14.2770	0.9501	0.5330	-16.4470	0.9506	0.5351	-17.0951	0.9514	0.5379	-17.1418	0.9512	0.5471	-22.2512
Benzaldehyde																
HF	DZSPDN	0.9444	0.5495	-16.3998	0.9545	0.5756	-36.6268	0.9542	0.5750	-36.0240	0.9522	0.5771	-35.7963	0.9568	0.5920	-43.3947
	7-*s*	0.9446	0.5537	-18.0443	0.9543	0.5798	-39.6269	0.9205	0.5352	-21.0816	0.9513	0.5800	-38.1694	0.9566	0.5936	-45.5156

Continued on next page

Table S4 – continued from previous page

Basis set		R^2	m	b	R^2	m	b	R^2	m	b	R^2	m	b	R^2	m	b
Electronic/Nuclear		6-311G			6-311G(d,p)			6-311G++(d,p)			cc-pVDZ			aug-cc-pVDZ		
DFT	DZSPDN	0.9261	0.5759	-28.0047	0.9544	0.6164	-55.0251	0.9515	0.6151	-54.0478	0.9543	0.6209	-55.4989	0.9602	0.6361	-63.2443
	7-*s*	0.9258	0.5806	-29.5610	0.9539	0.6192	-56.7533	0.9511	0.6172	-55.5178	0.9509	0.6204	-55.7674	0.9595	0.6378	-64.5939
MP2	DZSPDN	0.9018	0.6148	-42.6525	0.9377	0.6578	-71.4174	0.9339	0.6565	-70.4362	0.9377	0.6621	-71.7197	0.9483	0.6769	-79.4041
	7-*s*	0.9029	0.6146	-42.3181	0.9339	0.6550	-70.8801	0.9337	0.6594	-72.3210	0.9364	0.6705	-75.6906	0.9487	0.6794	-81.1181
Ketone																
HF	DZSPDN	0.9561	0.5310	-1.0599	0.9640	0.5453	-15.3881	0.9615	0.5412	-13.7173	0.9717	0.5506	-15.8570	0.9604	0.5375	-12.7531
	7-*s*	0.9540	0.5375	-3.3096	0.9713	0.5481	-17.5867	0.9679	0.5454	-16.4019	0.9701	0.5546	-18.4616	0.9630	0.5431	-16.1783
DFT	DZSPDN	0.9624	0.5114	5.2473	0.9676	0.5352	-13.0175	0.9649	0.5313	-11.3920	0.9678	0.5404	-13.8039	0.9640	0.5351	-13.4862
	7-*s*	0.9612	0.5163	3.7749	0.9675	0.5383	-14.7005	0.9654	0.5341	-12.9618	0.9679	0.5434	-15.3674	0.9649	0.5380	-15.0979
MP2	DZSPDN	0.9623	0.5108	5.5443	0.9602	0.5275	-9.9694	0.9600	0.5321	-11.8952	0.9641	0.5419	-14.5478	0.9614	0.5364	-14.1613
	7-*s*	0.9611	0.5154	4.1929	0.9616	0.5389	-15.0867	0.9602	0.5349	-13.4772	0.9634	0.5450	-16.1627	0.9610	0.5390	-15.6583
Ether																
HF	DZSPDN	0.9691	0.5219	-2.3083	0.9783	0.5536	-20.4722	0.9786	0.5464	-17.6377	0.9788	0.5587	-20.5188	0.9815	0.5364	-14.1103
	7-*s*	0.9756	0.5670	-17.9459	0.9792	0.5569	-22.9108	0.9772	0.5359	-14.5831	0.9695	0.5646	-23.7834	0.9706	0.5438	-18.0577
DFT	DZSPDN	0.9697	0.5390	-8.8930	0.9731	0.5194	-8.6114	0.9744	0.5266	-11.4906	0.9738	0.5363	-13.6700	0.9772	0.5077	-4.4293
	7-*s*	0.9698	0.5430	-9.7671	0.9691	0.5236	-10.5692	0.9736	0.5339	-14.8202	0.9740	0.5384	-14.8676	0.9780	0.5131	-6.9828
MP2	DZSPDN	0.9867	0.5648	-17.2163	0.9893	0.5587	-22.8702	0.9894	0.5518	-20.1773	0.9761	0.5524	-18.9183	0.9908	0.5402	-16.1050
	7-*s*	0.9869	0.5694	-18.3176	0.9885	0.5640	-25.3828	0.9887	0.5570	-22.6449	0.9755	0.5575	-21.3362	0.9899	0.5462	-18.8942
Carboxylic																
HF	DZSPDN	0.8651	0.5014	8.0053	0.9116	0.5392	-16.6596	0.9120	0.5319	-13.4556	0.9083	0.5455	-17.8811	0.9171	0.5301	-13.5467
	7-*s*	0.8889	0.5079	5.7547	0.9145	0.5333	-15.4866	0.9157	0.5261	-12.3301	0.9115	0.5388	-16.2548	0.9213	0.5250	-12.7198
DFT	DZSPDN	0.8772	0.4986	8.5158	0.9095	0.5042	-3.7821	0.9128	0.4994	-1.5176	0.9080	0.5094	-4.8084	0.9171	0.4982	-1.8926
	7-*s*	0.8767	0.4792	16.1546	0.8926	0.4787	5.8308	0.9156	0.4977	-1.2861	0.9114	0.5070	-4.2328	0.9206	0.4972	-1.9284
MP2	DZSPDN	0.8957	0.4983	8.5678	0.8356	0.5291	-13.6038	0.9025	0.4932	0.9996	0.8964	0.4946	0.9970	0.9020	0.4807	5.0334
	7-*s*	0.8919	0.5026	7.7105	0.9047	0.5056	-4.5393	0.9013	0.4922	0.9965	0.8959	0.5024	-2.3037	0.9003	0.4852	2.9548
Pyridine																
HF	DZSPDN	0.9529	0.6744	-64.9362	0.9537	0.7440	-101.3075	0.9503	0.7393	-99.1495	0.9514	0.7514	-103.0431	0.9425	0.7588	-108.5950
	7-*s*	0.9572	0.6910	-71.6408	0.9503	0.7460	-103.6245	0.9492	0.7466	-103.7763	0.9496	0.7583	-107.3614	0.9406	0.7638	-112.2325
DFT	DZSPDN	0.9565	0.6704	-62.8373	0.9542	0.7255	-93.4488	0.9500	0.7210	-91.3697	0.9519	0.7316	-94.7178	0.9439	0.7384	-99.8952
	7-*s*	0.9530	0.6726	-63.3376	0.9539	0.7325	-97.2437	0.9501	0.7257	-94.1423	0.9515	0.7373	-97.8302	0.9438	0.7442	-103.1564
MP2	DZSPDN	0.9582	0.6744	-64.4876	0.9568	0.7322	-96.4139	0.9517	0.7274	-94.1740	0.9416	0.7351	-96.4655	0.9341	0.7402	-100.9050
	7-*s*	0.9573	0.6805	-66.6169	0.9575	0.7388	-100.0324	0.9517	0.7340	-97.7726	0.9547	0.7452	-101.2763	0.9342	0.7455	-103.9064
Pyrazole																
HF	DZSPDN	0.9718	0.6527	-57.5179	0.9593	0.6725	-71.6886	0.9616	0.6711	-70.8217	0.9571	0.6760	-71.6074	0.9558	0.6907	-79.8525
	7-*s*	0.9729	0.6571	-59.2469	0.9597	0.6764	-74.7237	0.9591	0.6749	-73.7689	0.9573	0.6814	-75.1576	0.9555	0.6945	-82.9478
DFT	DZSPDN	0.9770	0.6481	-55.2046	0.9698	0.6702	-70.7534	0.9712	0.6683	-69.6498	0.9683	0.6739	-70.8883	0.9469	0.6177	-48.2255
	7-*s*	0.9776	0.6518	-56.4470	0.9698	0.6735	-72.9651	0.9702	0.6707	-71.4524	0.9679	0.6784	-73.4215	0.9660	0.6924	-81.4710
MP2	DZSPDN	0.9833	0.6595	-59.5348	0.9800	0.6839	-76.1938	0.9799	0.6810	-74.6833	0.9803	0.6894	-77.0574	0.9756	0.7016	-84.2477
	7-*s*	0.9834	0.6630	-60.7172	0.9801	0.6885	-78.9110	0.9796	0.6847	-77.0065	0.9800	0.6932	-79.3274	0.9751	0.7062	-86.9213
Sulfoether																
HF	DZSPDN	0.9739	0.4392	22.3094	0.9895	0.4829	-6.9551	0.9888	0.4800	-5.7801	0.9922	0.4847	-7.4730	0.9912	0.4489	7.4633
	7-*s*	0.9733	0.4373	24.3415	0.9899	0.4845	-8.2168	0.9892	0.4817	-7.0877	0.9926	0.4854	-8.2623	0.9930	0.4742	-4.1307
DFT	DZSPDN	0.9696	0.4184	30.5505	0.9863	0.4622	1.7672	0.9860	0.4599	2.7101	0.9896	0.4645	1.0074	0.9910	0.4558	4.0904
	7-*s*	0.9690	0.4170	32.4002	0.9872	0.4636	1.0036	0.9856	0.4609	2.1176	0.9901	0.4647	0.7774	0.9911	0.4558	3.9588
MP2	DZSPDN	0.9825	0.4666	11.0970	0.9925	0.5040	-16.1878	0.9896	0.4789	-5.3440	0.9953	0.5056	-16.6162	0.9943	0.4925	-11.6640
	7-*s*	0.9823	0.4648	13.2047	0.9923	0.5079	-18.3046	0.9888	0.4833	-7.6649	0.9948	0.5091	-18.5261	0.9937	0.4962	-13.6475

Table S5: Mean absolute error (MAE), mean absolute deviation (MAD) and maximum absolute deviation (AD_{max}) (in kcal mol^{-1}) for calculated PAs using the $PA^{FG} = m^{FG}\ PA^{FG}_{KT} + b^{FG}$ equations for each functional group corresponding to the 6-311G/DZSPDN combination of electronic/nuclear basis sets.

Functional group	HF geometry			DFT geometry			MP2 geometry		
	MAE^{FG}	MAD^{FG}	AD^{FG}_{max}	MAE^{FG}	MAD^{FG}	AD^{FG}_{max}	MAE^{FG}	MAD^{FG}	AD^{FG}_{max}
Amine	0.93	0.58	3.15	0.97	0.63	3.22	0.91	0.54	2.99
Aniline	1.30	0.71	3.91	1.28	0.73	3.84	1.31	0.72	3.49
Ester	0.47	0.36	1.36	0.49	0.32	1.79	0.46	0.32	1.16
Alcohol	1.43	0.94	5.85	1.35	0.16	5.55	1.26	0.84	5.45
Amide	1.07	0.64	3.10	1.25	0.69	3.30	1.10	0.66	3.42
Aldehyde	1.40	0.74	2.58	1.75	0.77	2.86	1.63	0.73	2.65
Benzaldehyde	0.68	0.45	2.17	0.72	0.54	2.78	0.86	0.63	3.08
Ketone	1.09	0.78	3.34	1.06	0.66	2.78	1.07	0.63	2.74
Ether	0.77	0.59	1.91	0.77	0.54	1.82	0.50	0.30	1.53
Carboxylic acid	1.76	1.01	3.65	1.73	0.89	3.64	1.66	0.75	3.14
Pyridine	1.35	0.96	5.75	1.31	0.89	5.76	1.26	0.90	5.39
Pyrazole	1.52	0.86	4.74	1.41	0.81	3.97	1.18	0.68	3.48
Sulfoether	0.54	0.28	1.23	0.55	0.33	1.28	0.41	0.29	0.94
Average	1.10	0.68	—	1.13	0.61	—	1.05	0.62	—

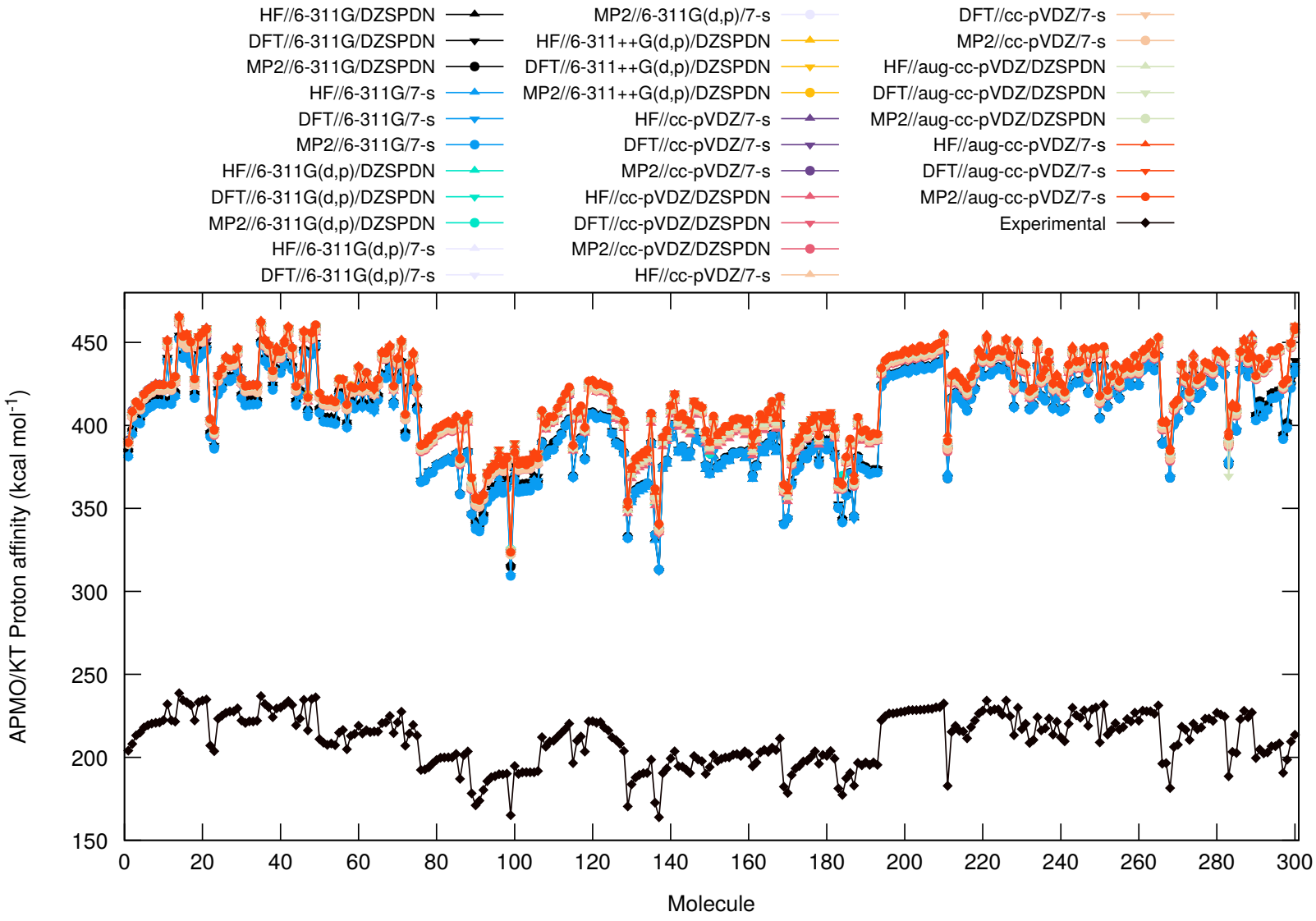


Figure S1: Experimental (PA_{exp}) and APMO/KT (PA_{KT}) proton affinities for the 300 organic molecules of the test set using HF, DFT(B3LYP) and MP2 geometries with 10 combinations of electronic/nuclear basis sets.

Table S6: Comparison of the performance of APMO/PP2 method and APMO/KT-SC-FG scheme on the calculation of proton affinities of 139 neutral organic molecules. Values in parenthesis correspond to the difference with respect to experimental data. (kcal mol^{-1}).

	Molecule	PA_{exp}	PA_{PP2}		$PA_{KT}^{SC\text{-}FG}$	
	Amine					
1	NH_3	204.02	203.01	(1.01)	204.72	(0.70)
2	$CHF_2CH_2NH_2$	208.05	207.99	(0.06)	210.99	(2.94)
3	$CH_2FCH_2NH_2$	213.19	213.26	(0.07)	214.37	(1.18)
4	CH_3NH_2	214.87	214.30	(0.56)	214.23	(0.64)
5	(c-C_3H_5)NH_2	216.20	216.45	(0.25)	217.00	(0.80)
6	$CH_3CH_2NH_2$	217.97	217.93	(0.04)	217.47	(0.51)
7	$CH_2(CH_3)CH_2NH_2$	219.30	218.72	(0.58)	219.64	(0.34)
8	$CH_3(CH_2)_2NH_2$	219.36	219.63	(0.27)	218.69	(0.67)
9	$CH_3(CH_2)_3NH_2$	220.24	220.62	(0.37)	219.33	(0.91)
10	$CH_3(CH_2)_4NH_2$	220.72	221.16	(0.43)	219.67	(1.05)
11	$(CH_3)_2CHNH_2$	220.79	220.67	(0.12)	220.23	(0.56)
12	$(CH_3)_2CHCH_2NH_2$	221.03	221.40	(0.37)	220.20	(0.83)
13	(c-C_6H_{11})CH_2NH_2	221.50	222.55	(1.05)	222.43	(0.93)
14	$CH_3(CH_2)_6NH_2$	221.56	221.63	(0.07)	219.96	(1.60)
15	$CH_3(CH_2)_5NH_2$	221.68	221.44	(0.24)	219.86	(1.82)
16	$CH_3(CH_2)_7NH_2$	222.01	221.75	(0.26)	220.02	(1.99)
17	$CH_3CH_2(CH_3)CHNH_2$	222.20	222.39	(0.19)	221.82	(0.38)
18	$CH_3(CH_2)_8NH_2$	222.28	221.83	(0.45)	220.06	(2.21)
19	$CH_3(CH_2)_9NH_2$	222.40	221.67	(0.73)	219.97	(2.43)
20	$(CH_3)_3CNH_2$	223.26	224.37	(1.11)	222.94	(0.31)
21	$(C_6H_{11})NH_2$	223.33	224.14	(0.81)	222.81	(0.51)
22	$CH_3CH_2C(CH_3)_2NH_2$	224.14	224.66	(0.52)	224.28	(0.14)
23	$(CH_3)_2NH$	222.16	221.98	(0.18)	221.59	(0.57)
24	$CH_3CH_2NHCH_3$	225.19	224.98	(0.21)	224.45	(0.74)
25	$(CH_3)_2CHNHCH_3$	227.61	227.30	(0.31)	226.92	(0.68)
26	$(CH_3CH_2)_2NH$	227.63	227.71	(0.08)	227.12	(0.51)
27	$CH(CH_3)_2NHCH_2CH_3$	229.45	229.84	(0.39)	229.41	(0.04)
28	$(C_3H_7)_2NH$	230.00	230.48	(0.48)	229.16	(0.83)
29	$(C_4H_9)_2NH$	231.48	232.07	(0.59)	230.23	(1.24)
30	(sec-C_4H_9)$_2NH$	234.39	235.02	(0.63)	233.77	(0.63)
31	(t-C_4H_9)$_2NH$	236.11	236.32	(0.21)	235.98	(0.13)
32	$(CH_3)_3N$	226.79	226.64	(0.16)	227.28	(0.49)
33	$CH_3CH_2N(CH_3)_2$	229.50	229.55	(0.05)	230.03	(0.53)
34	$(CH_3)_2N$(n-C_3H_7)	230.10	230.86	(0.76)	231.02	(0.92)
35	$(CH_3)_2CHCH_2N(CH_3)_2$	231.52	231.38	(0.14)	231.78	(0.25)
36	$(C_4H_7)N(CH_3)_2$	231.64	231.65	(0.00)	231.56	(0.08)
37	$(CH_3)_2CHN(CH_3)_2$	231.98	231.78	(0.20)	232.38	(0.40)
38	$(C_2H_5)_2NCH_3$	232.10	232.11	(0.01)	232.57	(0.47)
39	(c-C_6H_{11})$CH_2N(CH_3)_2$	233.17	232.34	(0.83)	233.89	(0.72)
40	(sec-C_4H_9)$(CH_3)_2N$	233.25	233.30	(0.05)	233.50	(0.25)
41	$(C_2H_5)_2N(C_3H_7)$	233.94	233.41	(0.53)	236.32	(2.38)
42	(t-C_4H_9)$(CH_3)_2N$	234.13	234.18	(0.05)	234.78	(0.65)

Continued on next page

	Molecule	PA_{exp}	PA_{PP2}		$PA_{KT}^{SC\text{-}FG}$	
43	$(C_2H_5)_3N$	234.66	234.09	(0.56)	235.26	(0.61)
44	$(t\text{-}C_5H_{11})(CH_3)_2N$	234.82	235.76	(0.93)	235.95	(1.12)
45	$(c\text{-}C_6H_{11})N(CH_3)_2$	235.09	234.73	(0.36)	234.65	(0.43)
46	$(C_3H_7)_3N$	236.90	237.12	(0.22)	237.86	(0.96)
47	$(n\text{-}C_4H_9)_3N$	238.65	239.13	(0.49)	239.26	(0.61)
	Amide					
48	$HCONH_2$	196.50	195.43	(1.07)	197.24	(0.74)
49	$HCONHCH_3$	203.47	202.52	(0.94)	203.99	(0.53)
50	CH_3CONH_2	206.41	206.19	(0.21)	205.43	(0.97)
51	$CH_3CH_2CONH_2$	209.42	208.84	(0.57)	207.75	(1.67)
52	$(CH_3)_2CHCNH_2O$	209.99	210.69	(0.70)	209.54	(0.45)
53	$n\text{-}C_3H_7NHCHO$	209.94	210.12	(0.18)	209.95	(0.01)
54	$(CH_3)_2CHCONH_2$	210.40	211.15	(0.75)	210.27	(0.13)
55	$(CH_3)_2NCHO$	212.12	210.41	(1.71)	210.30	(1.82)
56	$CH_3CONHCH_2$	212.36	211.46	(0.90)	211.14	(1.22)
57	$(CH_3)_3CONH_2$	212.50	213.41	(0.91)	211.81	(0.69)
58	$CH_3CONHC_2H_5$	214.63	214.31	(0.32)	213.53	(1.10)
59	$CH_3CON(CH_3)_2$	217.02	218.11	(1.09)	216.93	(0.09)
60	$CH_3CH_2CH_2CON(CH_3)_2$	220.29	219.96	(0.33)	218.94	(1.35)
61	$C_3H_7CON(CH_3)_2$	220.77	221.02	(0.25)	219.86	(0.91)
62	$CH_3CON(C_2H_5)_2$	221.18	220.96	(0.21)	220.30	(0.88)
63	$(CH_3)_3CCON(CH_3)_2$	221.58	221.67	(0.09)	221.17	(0.41)
64	$(CH_3)_3CCH_2CON(CH_3)_2$	221.73	222.63	(0.90)	221.59	(0.14)
	Ester					
65	$HCOOCH_3$	187.02	186.60	(0.43)	186.79	(0.23)
66	$HCO_2C_2H_5$	191.06	191.49	(0.43)	190.56	(0.50)
67	$HCO_2(n\text{-}C_3H_7)$	192.38	193.01	(0.63)	191.75	(0.63)
68	$HCO_2(n\text{-}C_4H_9)$	192.64	193.39	(0.75)	192.39	(0.25)
69	$HCOOCH(CH_3)_2$	193.91	195.73	(1.82)	194.42	(0.51)
70	$CH_3CO_2CH_3$	196.37	196.51	(0.14)	195.63	(0.74)
71	$C_2H_5COOCH_3$	198.42	197.62	(0.81)	198.38	(0.05)
72	$CH_3COOCH_2CH_3$	199.74	200.67	(0.93)	198.87	(0.87)
73	$C_3H_7COOCH_3$	199.95	201.81	(1.86)	199.79	(0.17)
74	$C_3H_7COOCH_3$	199.90	198.97	(0.93)	199.90	(0.01)
75	$i\text{-}C_3H_7COOCH_3$	199.95	198.97	(0.99)	200.79	(0.84)
76	$(c\text{-}C_3H_5)COOCH_3$	201.29	200.82	(0.47)	201.11	(0.19)
77	$(t\text{-}C_4H_9)COOCH_3$	202.01	201.62	(0.38)	202.68	(0.67)
78	$CH_3CHCHCOOCH_3$	203.49	203.75	(0.26)	203.57	(0.08)
	Alcohol					
79	CH_3OH	180.28	180.57	(0.28)	179.87	(0.41)
80	CHF_2CH_2OH	173.85	172.47	(1.38)	175.39	(1.53)
81	CH_2FCH_2OH	171.03	170.87	(0.16)	172.68	(1.65)
82	CH_3CH_2OH	185.56	185.23	(0.33)	185.87	(0.31)
83	$(CH_3)_2CH_2OH$	189.70	190.06	(0.36)	188.94	(0.76)
84	$CH_3(CH_2)_2OH$	187.98	187.41	(0.57)	187.67	(0.31)
85	$CH_3(CH_2)_3OH$	188.62	188.83	(0.20)	188.73	(0.11)
86	$CH_3(CH_2)_4OH$	190.01	189.63	(0.38)	189.31	(0.70)
87	$CH_3(CH_2)_5OH$	190.97	190.00	(0.96)	189.57	(1.39)

Continued on next page

	Molecule	PA_{exp}	PA_{PP2}		$PA_{KT}^{SC\text{-}FG}$	
88	$CH_3(CH_2)_6OH$	190.97	190.23	(0.73)	189.73	(1.24)
89	$CH_3(CH_2)_7OH$	190.97	190.38	(0.59)	189.83	(1.14)
90	(c-C_6H_{11})CH_2OH	191.71	191.59	(0.11)	191.49	(0.22)
91	$CH_3CH_2CH(OH)CH_3$	194.79	194.86	(0.07)	193.46	(1.32)
92	i-$CH_3(CH_2)_2OH$	189.77	191.45	(1.68)	191.51	(1.74)
93	$(CH_3)_3CCH_2OH$	190.13	189.59	(0.54)	190.69	(0.56)
94	(c-C_5H_9)OH	191.00	191.41	(0.41)	191.98	(0.98)
	Ether					
95	CH_3OCH_3	189.29	189.17	(0.12)	189.01	(0.28)
96	$CH_3CH_2OCH_3$	193.26	193.95	(0.69)	193.83	(0.57)
97	(n-C_3H_7)OCH_3	194.77	194.74	(0.03)	195.06	(0.29)
98	(C_4H_9)OCH_3	196.06	196.79	(0.73)	196.11	(0.05)
99	$(C_2H_5)_2O$	197.99	198.04	(0.05)	198.10	(0.11)
100	$(CH_3)_2CHOCH_3$	197.49	199.31	(1.82)	198.38	(0.89)
101	(c-C_6H_{11})CH_2OCH_3	199.21	198.89	(0.32)	198.52	(0.69)
102	$(C_3H_7)_2O$	200.26	201.02	(0.76)	200.66	(0.40)
103	(c-C_6H_{11})OCH_3	200.88	201.56	(0.67)	201.13	(0.25)
104	$(C_4H_9)_2O$	203.63	202.94	(0.70)	202.12	(1.52)
105	$(CH_3)_2CHOCH_2CH_3$	201.41	202.59	(1.18)	202.26	(0.85)
106	(n-C_5H_{11})$_2O$	203.80	204.87	(1.07)	203.31	(0.49)
	Aldehyde					
107	CH_2O	170.39	167.06	(3.33)	173.04	(2.65)
108	CH_3CHO	183.68	183.99	(0.31)	183.51	(0.17)
109	CH_3CH_2CHO	187.86	187.73	(0.13)	186.36	(1.50)
110	n-C_3H_7CHO	189.46	189.38	(0.08)	187.34	(2.12)
111	n-C_4H_9CHO	190.39	190.26	(0.13)	187.85	(2.54)
112	$(CH_3)_2CHCOH$	190.56	191.25	(0.69)	188.28	(2.28)
	Ketone					
113	$(CH_3)_2CO$	194.07	193.98	(0.09)	195.39	(1.31)
114	(c-C_4H_6O)	194.60	195.90	(1.30)	196.69	(2.09)
116	$CH_3COC_2H_5$	197.73	196.61	(1.12)	197.24	(0.49)
115	(c-C_5H_8O)	196.87	197.73	(0.86)	197.73	(0.86)
117	n-$C_3H_7COCH_3$	199.02	198.04	(0.98)	198.19	(0.83)
118	$(CH_3)_2CHCOCH_3$	199.88	200.98	(1.10)	199.95	(0.07)
119	$(C_2H_5)_2CO$	200.00	198.80	(1.20)	200.25	(0.25)
123	$(C_3H7)_2CO$	201.96	199.61	(2.35)	201.27	(0.69)
126	(c-$C_6H_{10}O$)	203.60	203.08	(0.52)	201.57	(2.03)
121	$CH_3CH_2CH_2COCH_2CH_3$	201.53	200.46	(1.07)	201.64	(0.11)
120	$(CH_3)_3COCH_3$	200.79	199.41	(1.38)	201.92	(1.13)
122	p-$(CH_3)C_6H_9O$	201.94	204.00	(2.06)	202.15	(0.21)
128	(c-$C_7H_{12}O$)	204.50	203.94	(0.56)	202.32	(2.18)
127	(c-C_3H_5)$COCH_3$	204.33	203.44	(0.88)	203.14	(1.19)
124	(c-$C_8H_{14}O$)	203.01	203.98	(0.97)	203.59	(0.58)
125	(i-C_3H_7)$_2CO$	203.23	204.22	(0.99)	204.46	(1.23)
129	(t-C_4H_9)$_2CO$	205.86	205.48	(0.37)	207.10	(1.25)
	Carboxylic					
130	HCOOH	177.34	174.87	(2.47)	179.72	(2.38)
131	CH_2FCOOH	182.94	184.07	(1.14)	185.63	(2.70)

Continued on next page

	Molecule	PA_{exp}	PA_{PP2}		$PA_{KT}^{SC\text{-}FG}$	
132	CH_3COOH	187.31	186.98	(0.33)	187.63	(0.32)
133	C_2H_5COOH	190.54	191.49	(0.96)	193.70	(3.16)
134	$(CH_3)_2CCOOH$	195.20	195.34	(0.15)	195.82	(0.63)
135	(c-C_4H_7)COOH	195.41	195.65	(0.24)	194.11	(1.30)
136	(c-C_5H_9)COOH	195.41	196.30	(0.89)	194.61	(0.80)
137	$(CH_3)_2CCHCOOH$	196.70	197.39	(0.69)	198.63	(1.93)
138	(c-C_6H_{11})COOH	196.89	195.94	(0.96)	194.54	(2.35)
139	$CH_3(CH)_2COOH$	196.89	196.25	(0.64)	195.38	(1.51)

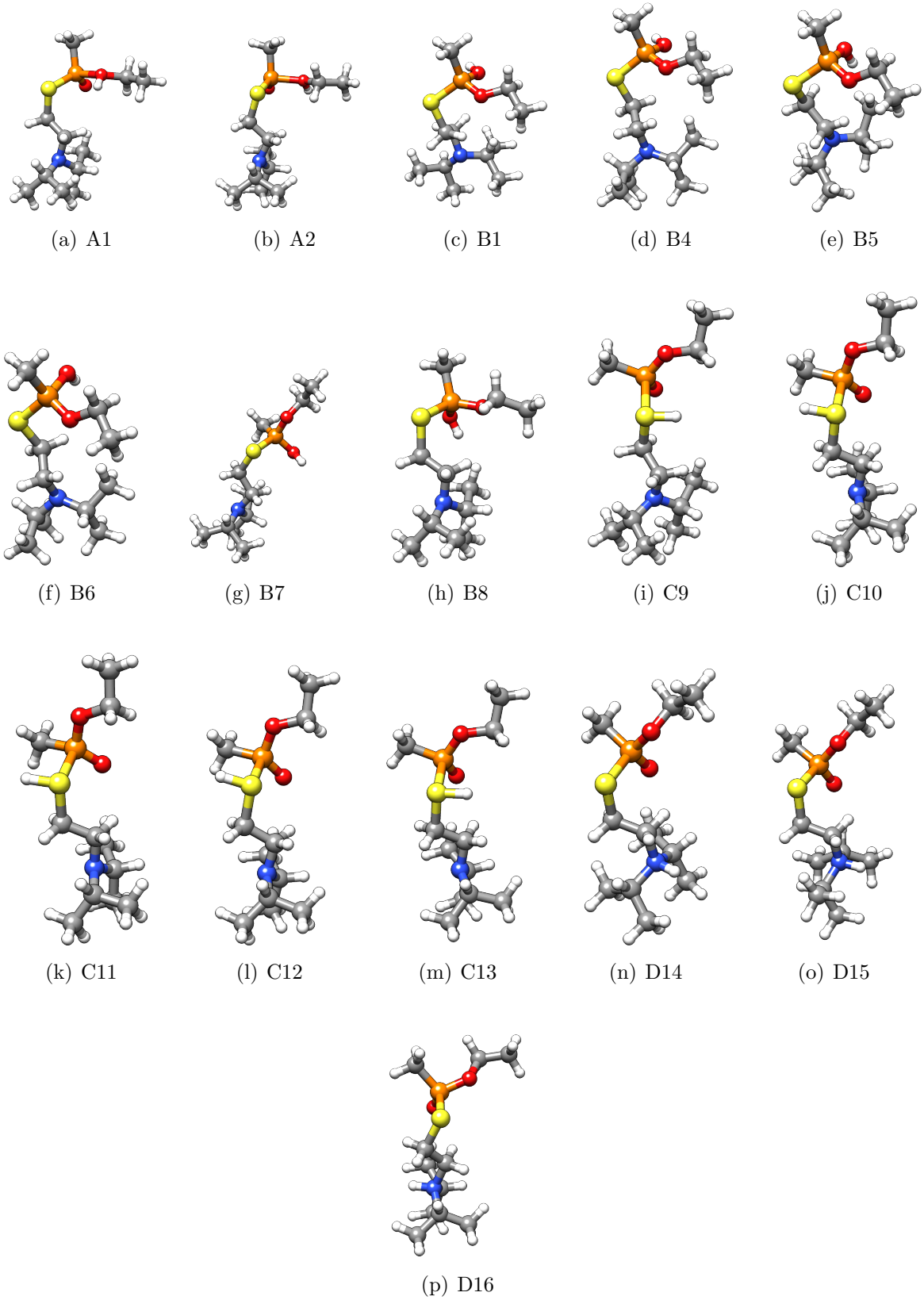
Table S7: Proton Affinity for protonation products of the Nerve Agent VX (kcal mol^{-1}). APMO/KT calculations were performed with the 6-311G electronic and DZSPDN nuclear basis sets. PA_{KT}^{FG} were calculated using Equations 19 for different functional groups: Ether (A1-A2), Ester (B3-B8), Sulfoether (C9-C12) and Amine (D14-D16). Structures are presented in Figure S2.

Protonation		B3LYP/6-31G(d) geometry			B3LYP/6-311++G(d,p) geometry		
site	Molecule	PA_{ad} [a]	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$	PA_{ad} [a]	PA_{KT}^{SC}	$PA_{KT}^{SC\text{-}FG}$
O1	A1	202.64	209.18	207.02	204.05	210.10	207.93
O1	A2	202.31	210.85	208.67	203.38	212.04	209.86
O2	B3	224.58	217.04	223.38	225.80	217.65	224.13
O2	B4	224.74	217.11	223.47	225.73	217.65	224.13
O2	B5	224.69	218.02	224.58	225.12	218.33	224.95
O2	B6	224.57	218.50	225.16	225.29	218.64	225.32
O2	B7	225.33	218.33	224.95	225.97	218.84	225.57
O2	B8	225.29	220.13	227.13	225.84	220.20	227.21
S3	C9	209.57	224.22	209.75	210.05	224.62	210.07
S3	C10	209.11	222.52	208.44	209.24	223.09	208.89
S3	C11	208.65	222.62	208.52	209.25	223.13	208.91
S3	C12	208.45	222.82	208.68	209.23	223.16	208.94
S3	C13	210.11	222.75	208.63	209.74	223.33	209.07
N4	D14	247.43	243.00	248.36	245.44	243.10	248.45
N4	D15	251.91	243.92	249.19	249.98	243.64	248.94
N4	D16	252.10	243.20	248.55	249.81	243.30	248.64

[a] PA_{ad}= $E(AH^+)$ - E(A)

Complete citations:

42. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. *Gaussian 09*, Revision D.01, 2013, Gaussian, Inc., Wallingford CT.



(a) A1 (b) A2 (c) B1 (d) B4 (e) B5

(f) B6 (g) B7 (h) B8 (i) C9 (j) C10

(k) C11 (l) C12 (m) C13 (n) D14 (o) D15

(p) D16

Figure S2: Structures of the protonation products of the Nerve Agent VX.