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Supporting Information

A Theoretical Evaluation of the pK_{HB} and ΔH°_{HB} Hydrogen-Bond Scales of Nitrogen Bases.

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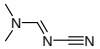
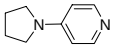
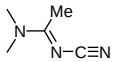
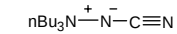
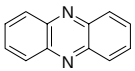
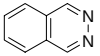
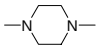
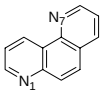
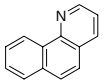
Supplementary Material. Experimental and calculated hydrogen-bond properties, pK_{HB} and ΔH°_{HB}, for the whole set of nitrogen compounds.

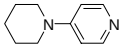
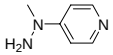
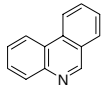
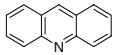
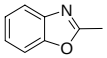
N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	p$K_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
1	Chloroacetonitrile		0.42	16.3	138.61	26.04	27.88	0.18	13.8
2	4-Chlorobenzonitrile		0.68	15.8	154.62	31.11	32.93	0.65	16.9
3	Acrylonitrile		0.71	17.5	159.06	30.66	32.65	0.67	16.7
4	Methylthiocyanate		0.73	16.6	157.23	30.32	32.26	0.63	16.5
5	Benzonitrile		0.80	17.5	164.91	32.42	34.32	0.84	17.7
6	2,6-Dimethylbenzonitrile		0.86	18.1	167.11	34.25	36.17	0.97	18.9
7	Allylcyanide		0.87	17.8	165.25	32.20	34.18	0.83	17.7
8	Acetonitrile		0.89	19.3	164.38	32.19	34.28	0.82	17.7
9	Propionitrile		0.93	18.2	168.54	32.95	35.02	0.91	18.2
10	Isobutyronitrile		0.98	18.1	170.77	33.71	35.87	0.98	18.7
11	4-Methoxybenzonitrile		0.99	18.1	175.60	34.93	36.81	1.10	19.3
12	Trimethylacetonitrile		0.99	18.5	171.63	34.65	36.62	1.04	19.2
13	4-Dimethylaminobenzonitrile		1.26	20.5	190.33	37.95	40.04	1.43	21.3
14	Dimethylcyanamide		1.51	22.4	187.88	38.70	40.44	1.46	21.5
15	1-Piperidinecarbonitrile		1.58	21.7	193.48	39.75	41.75	1.58	22.3
16	Diethylcyanamide [a]		1.61	21.9	190.35	39.64	41.67	1.54	22.3
17	*trans*-3-Dimethylaminoacrylonitrile		1.70	23.5	202.92	41.50	43.40	1.78	23.3
18	N^1,N^1-Dimethyl-N^2-cyanoformamidine		2.03	24.5	213.74	43.43	45.85	2.01	24.8
19	3,5-Dichloropyridine		0.81	23.9	123.15	40.49	43.08	0.91	23.1
20	3-Chloropyridine		1.30	27.2	141.27	45.43	48.12	1.39	26.2
21	3-Bromopyridine		1.35	24.8	140.84	44.96	47.69	1.36	26.0
22	3-Fluoropyridine		1.35	25.4	143.20	45.86	48.62	1.44	26.6
23	Pyridine		1.86	29.6	160.76	50.76	53.61	1.92	29.6
24	Quinoline		1.90	30.1	153.35	51.68	54.59	1.90	30.2
25	Isoquinoline		1.93	29.7	163.03	51.97	54.65	2.01	30.3
26	2-Methylpyridine		2.01	30.5	159.50	52.80	55.80	2.03	31.0
27	3-Methylpyridine		2.03	30.0	167.34	52.65	55.33	2.10	30.7
28	4-Methylpyridine		2.10	30.8	168.79	52.86	55.67	2.13	30.9
29	3,5-Dimethylpyridine		2.18	31.9	170.79	53.79	56.65	2.21	31.5

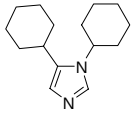
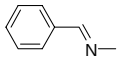
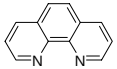
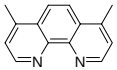
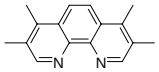
N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
30	2,4-Dimethylpyridine		2.21	31.8	166.50	54.92	57.81	2.23	32.2
31	4-Aminopyridine		2.52	32.7	182.20	57.35	60.04	2.54	33.6
32	4-Methylaminopyridine		2.69	33.5	188.24	59.61	61.96	2.74	34.8
33	4-*N*,*N*-Dimethylaminopyridine		2.77	34.1	191.07	59.67	62.26	2.77	35.0
34	4-Pyrrolidinopyridine		2.93	36.3	195.32	60.46	63.41	2.86	35.7
35	2-Methylpyrroline		2.56	34.2	176.82	57.34	60.10	2.48	33.6
36	5-Bromo-1-methylimidazole		2.22	30.5	176.81	51.37	54.13	2.12	29.9
37	1-Methylimidazole		2.70	34.0	196.01	56.15	59.00	2.61	32.9
38	3,5-Difluorobenzylamine [a]		1.28	29.0	113.08	48.58	52.17	1.30	28.7
39	3-Fluorobenzylamine [a]		1.58	29.6	127.70	51.38	54.96	1.62	30.5
40	Benzylamine [a]		1.88	31.1	142.86	54.27	57.82	1.95	32.2
41	3-Methylbenzylamine [a]		1.97	31.7	146.83	55.17	58.63	2.05	32.7
42	*t*Butylamine		2.23	34.2	162.31	56.75	60.59	2.30	33.9
43	Ethylamine [a]		2.28	33.8	167.87	55.86	59.67	2.30	33.4
44	1,2,3,6-Tetrahydropyridine [a]		2.16	32.1	155.56	57.24	60.56	2.26	33.9
45	Dimethylamine [a]		2.23	35.1	155.01	56.62	60.30	2.22	33.7
46	*N*-Methylethylamine [a]		2.26	34.7	153.72	57.39	60.95	2.25	34.2
47	Piperidine [a]		2.34	36.0	152.43	58.48	61.76	2.30	34.6
48	Pyrrolidine [a]		2.56	36.1	160.02	59.43	62.73	2.44	35.2
49	Azetidine		2.57	35.7	163.92	59.90	63.36	2.51	35.6
50	*N*,*N*-Dimethylbenzylamine [a]		1.61	31.9	110.74	54.13	57.40	1.61	32.0
51	*N*,*N*-Dimethylpropargylamine [a]		1.63	30.3	131.62	51.96	55.38	1.69	30.7
52	*N*,*N*-Dimethylallylamine [a]		1.93	32.8	131.36	55.39	58.90	1.90	32.9
53	3-Chloroquinuclidine		1.96	34.1	133.98	55.61	58.70	1.94	32.8
54	1-Methyl-1,2,3,6-tetrahydropyridine		1.98	32.5	140.60	55.54	58.70	2.00	32.8

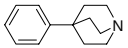
N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
55	*N*-Methylpiperidine		2.11	34.0	135.53	57.63	60.85	2.08	34.1
56	Trimethylamine		2.11	33.5	140.68	56.54	59.78	2.07	33.4
57	*N*,*N*-Dimethylethylamine [a]		2.17	34.5	138.40	57.09	60.42	2.08	33.8
58	*N*-Methylpyrrolidine		2.25	34.8	138.45	58.36	61.41	2.15	34.4
59	Quinuclidine		2.67	37.7	157.73	61.95	65.02	2.57	36.7
60	N^1,N^1-Dimethyl-N^2-cyanoacetamidine		2.24		215.48	45.83	47.56	2.17	25.9
61	Tri-*n*butylammonium cyanamidate		3.24		248.79	57.62	59.34	3.24	33.2
62	2-Ethylpyridine [a]		1.90	34.0	155.57	53.15	56.02	2.01	31.1
63	2-*i*Propylpyridine [a]		1.76		146.20	51.61	54.60	1.82	30.2
64	2-*t*Butylpyridine [a]		1.41	31.7	139.47	49.06	52.19	1.60	28.8
65	2,6-Dimethylpyridine		2.09	33.3	155.66	55.03	57.83	2.13	32.2
66	2,4,6-Trimethylpyridine		2.28	35.4	163.49	56.38	59.44	2.29	33.2
67	2-Fluoropyridine		0.94	24.5	154.10	39.23	41.79	1.14	22.3
68	2-Chloropyridine		1.07	24.1	152.37	39.91	42.53	1.17	22.8
69	2-Bromopyridine		1.04	23.7	150.62	39.60	42.19	1.13	22.6
70	2,6-Di-*t*butylpyridine		-0.54		98.39	36.37	40.35	0.40	21.5
71	1,2,2,6,6-Pentamethylpiperidine		1.25	34.0	116.92	55.24	58.58	1.74	32.7
72	[Triazine-$(CCl_4)_2$]		0.31 [b]	19.8	99.91	34.44	36.72	0.30	19.2
73	[Pyrazine-CCl_4]		0.94 [b]	22.6	123.52	41.41	44.08	0.97	23.8
74	[Pyrimidine-CCl_4]		1.06 [b]	23.9	130.02	42.09	44.77	1.07	24.2
75	[5-Bromopyrimidine-CCl_4]		0.59 [b]		112.33	37.63	40.08	0.62	21.3
76	[Phenazine-CCl_4]		1.22 [b]		119.30	46.26	48.76	1.22	26.6

N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
77	[Pyridazine-CCl_4]		1.65 [b]	27.9	165.38	43.81	46.33	1.54	25.1
78	[Phtalazine-CCl_4]		1.97 [b]		177.12	46.96	49.32	1.85	27.0
79	[2,5-Dimethylpyrazine-CCl_4]		1.29 [b]	26.6	129.93	45.69	48.28	1.29	26.3
80	[4,6-Dimethylpyrimidine-CCl_4]		1.47 [b]	27.8	137.98	47.15	49.76	1.46	27.3
81	[*N*,*N*-Dimethylpiperazine-CCl_4]		1.88 [b]	32.9	123.00	55.27	58.24	1.81	32.5
82	[Hexamethylenetetramine-$(CCl_4)_3$]		1.33 [b]	26.2	100.99	48.59	51.05	1.17	28.1
83	Cyanamide		1.19		175.53	35.21	37.11	1.12	19.5
84	Imidazole		2.47		188.94	53.79	56.74	2.39	31.6
85	4-Methylimidazole		2.64		188.56	55.57	58.53	2.50	32.7
86	3-Methyl-4-bromopyrazole				137.26	44.82	47.23	1.31	25.7
87	Pyrazole				158.57	46.72	49.45	1.65	27.1
88	4-Methylpyrazole				164.69	48.32	50.91	1.81	28.0
89	3- Methylpyrazole				158.58	49.37	52.07	1.81	28.7
90	5- Methylpyrazole				168.20	49.36	52.05	1.91	28.7
91	3(5)- Methylpyrazole (weighted)				162.47	49.36	52.06	1.85	28.7

N°	Compound	Structure	Experimental			Theoretical			Calculated	
			pK_{HB}	-ΔH°_{HB}		-$V_{s,min}$	-$\Delta D_0^{(HF)}$	-$\Delta H^{\circ(HF)}$	p$K_{HB,calc}$	-$\Delta H^{\circ}_{HB,calc}$
92	3,5-Dimethylpyrazole					166.92	51.91	54.56	2.05	30.2
93	3,4,5-Trimethylpyrazole					170.33	53.28	55.83	2.17	31.0
94	2,4,5-Trimethyloxazole					165.87	52.53	55.04	2.08	30.5
95	[1,7-Phenanthroline-(CCl_4)]		Polyfunctional pK_t = 1.87		N_1	145.99	51.83	54.40	1.83	30.1
96	[Quinazoline--(CCl_4)]		Polyfunctional pK_t = 1.55		N_7	98.44	44.93	47.70	0.92	26.0
					N_1	129.75	45.65	48.15	1.29	26.3
97	[2-Cyanopyridine-(CCl_4)]		Polyfunctional pK_t = 0.85		N_3	137.61	44.47	47.00	1.30	25.6
					N_{sp^2}	127.34	34.87	37.43	0.60	19.7
98	[3-Cyanopyridine-(CCl_4)]		Polyfunctional pK_t = 1.00		N_{sp}	157.01	29.77	31.53	0.59	16.0
					N_{sp^2}	116.42	40.36	42.92	0.83	23.0
99	[4-Cyanopyridine-(CCl_4)]		Polyfunctional pK_t = 1.05		N_{sp}	145.06	29.15	30.80	0.43	15.6
					N_{sp^2}	117.86	41.99	44.62	0.94	24.1
100	[*N*,*N*-Dimethylaminoacetonitrile-(CCl_4)]		Polyfunctional pK_t = 1.02		N_{sp}	137.24	27.54	29.27	0.26	14.6
					N_{sp^3}	84.8	44.46	47.50	0.76	25.9
101	7,8-Benzoquinoline		1.16		N_{sp}	154.77	31.53	33.24	0.68	17.1
						121.61	45.84	48.81	1.22	26.7
102	Trichloroacetonitrile		-0.26			113.10	20.74	22.15	-0.41	10.2
103	4-Trifluoromethylbenzonitrile		0.54			143.44	29.08	30.85	0.41	15.6
104	*n*Pentanenitrile		0.89			171.91	33.26	35.46	0.96	18.4
105	Butyronitrile		0.89			170.35	33.58	35.64	0.96	18.6
106	*c*Propanenitrile		1.03			172.29	34.33	36.25	1.03	18.9
107	1-Pyrrolidinecarbonitrile		1.66			199.48	41.02	43.10	1.72	23.2
108	3-Aminopyridine		2.20			172.43	53.81	56.58	2.22	31.5
109	3-Ethylpyridine		2.01			167.35	52.47	55.30	2.09	30.7

N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
110	4-Chloropyridine		1.54		143.65	47.21	49.91	1.53	27.3
111	4-Phenylpyridine		1.96		163.93	52.15	54.88	2.03	30.4
112	4-Ethylpyridine		2.07		168.64	53.00	55.80	2.13	31.0
113	4-*t*Butylpyridine		2.11		171.29	53.45	56.19	2.19	31.2
114	4-Methoxypyridine		2.13		172.35	54.31	57.01	2.25	31.7
115	4-Piperidinopyridine		2.68		187.14	58.71	61.40	2.67	34.4
116	*N*-Methyl-*N*-pyridin-4-ylhydrazine		2.77		192.98	59.41	62.04	2.78	34.8
117	4-*N*,*N*-Diethylaminopyridine		2.89		192.48	59.34	62.15	2.77	34.9
118	3,4-Dimethylpyridine		2.24		173.57	54.06	56.88	2.25	31.6
119	Phenanthridine		1.87		152.78	51.45	54.27	1.88	30.0
120	Acridine		1.95		145.18	53.22	56.01	1.91	31.1
121	2-Vinylpyridine [a]		1.65		135.03	48.80	51.92	1.53	28.6
122	2-Phenylpyridine		1.41	27.6	141.72	47.53	50.44	1.53	27.7
123	2,6-Difluoropyridine		0.19	17.2	138.72	28.32	30.40	0.32	15.3
124	2-Aminopyridine		2.12		146.65	58.69	61.78	2.26	34.7
125	2-*N*-Methylaminopyridine [a]		2.11		148.09	57.34	60.58	2.19	33.9
126	2-*N*,*N*-Dimethylaminopyridine		1.61		131.56	48.79	51.70	1.50	28.5
127	*N*-Methylpyrazole		1.84		161.31	49.10	51.91	1.82	28.6
128	Oxazole		1.30		151.74	43.17	45.83	1.36	24.8
129	Isoxazole		0.81		155.30	36.07	38.54	0.96	20.3
130	Thiazole		1.37		148.94	44.07	46.80	1.39	25.4
131	Benzothiazole		1.29		139.30	43.49	46.01	1.25	24.9
132	2-Methylbenzoxazole		1.48		147.00	46.42	49.04	1.51	26.8
133	[1,2,3-Benzothiadiazole-CCl_4]		0.25		114.53	34.61	36.76	0.46	19.2

N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
134	1,5-Dicyclohexylimidazole		3.12		209.80	60.92	63.67	3.04	35.8
135	*N*-Vinylimidazole [a]		2.35		180.00	52.13	54.86	2.20	30.4
136	Tetramethylguanidine		3.20	37.52	193.39	64.04	66.90	3.06	37.81
137	*N*-Benzylidenemethylamine		1.49		133.63	50.04	53.24	1.60	29.4
138	*o*Phenanthroline		3.10	36.1	248.83	52.01	54.66	2.89	30.3
139	4,7- Dimethyl-*o*phenanthroline		3.34		260.72	54.63	57.22	3.17	31.9
140	3,4,7,8-Tetramethyl-*o*phenanthroline		3.46		267.36	55.94	58.53	3.32	32.7
141	Methylamine		2.20	35.1	168.98	55.61	59.68	2.30	33.4
142	3,5-Dichlorobenzylamine [a]		1.27	27.8	111.34	48.29	51.80	1.26	28.5
143	*n*Propylamine [a]		2.19		167.00	56.11	59.75	2.31	33.4
144	*i*Propylamine [a]		2.22		163.96	56.37	59.97	2.29	33.5
145	*n*Butylamine [a]		2.21		167.64	56.67	60.18	2.35	33.7
146	3-Trifluoromethylbenzylamine [a]		1.43	28.4	116.19	49.83	53.37	1.41	29.5
147	1-Aminoadamantane		2.31		164.17	56.55	60.30	2.31	33.7
148	*c*Propylamine[a]		1.74		148.50	51.60	55.21	1.84	30.6
149	Allylamine [a]		1.94		157.49	53.93	57.52	2.08	32.0
150	Propargylamine [a]		1.60	30.6	149.96	50.82	54.20	1.81	30.0
151	3-Trifluoromethyl-*N*,*N*-dimethylbenzylamine [a]		1.16	28.6	89.35	50.66	53.83	1.18	29.8
152	3-Fluoro-*N*,*N*-dimethylbenzylamine [a]		1.27	29.7	98.11	52.03	55.21	1.36	30.6
153	2-Methylaziridine [a]		2.28		174.15	56.53	59.81	2.41	33.4
154	Di-*i*propylamine		2.00	36.0	144.28	57.43	61.02	2.16	34.2

N°	Compound	Structure	Experimental		Theoretical			Calculated	
			pK_{HB}	$-\Delta H^{\circ}_{HB}$	$-V_{s,min}$	$-\Delta D_0^{(HF)}$	$-\Delta H^{\circ(HF)}$	$pK_{HB,calc}$	$-\Delta H^{\circ}_{HB,calc}$
155	Hexamethyleneimine [a]		2.26		146.81	56.91	60.29	2.15	33.7
156	*N*-Methylbenzylamine [a]		1.84	33.5	127.79	56.36	59.81	1.92	33.4
157	N-Methylpropargylamine [a]		1.69	29.3	141.84	52.67	55.99	1.84	31.1
158	4-Phenylquinuclidine [a]		2.46		151.36	60.90	63.69	2.44	35.8

[a] Theoretical properties correspond to average weighted values for the different stable isomers of the monomer. [b] statistically corrected by log(n) ; n is the number of equivalent nitrogen atoms in the molecule.