pK_a values of weak acids in MeCN from

The Acidity of Weak NH Acids: Expanding the pKa Scale in Acetonitrile

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Table 2. Acidities in different solvents and the gas phase.

Compound	**CAS RN**	**pK_a (MeCN)**[a]	**pK_a (DMSO)**	**pK_a (H_2O)**	**Exp. GA,**[b] **kJ mol^{-1}**	**Calc. GA,**[c] **kJ mol^{-1}**
2,3,5,6-Cl_4-Aniline	3481-20-7	33.51	21.0[18]	19.22[19]		1426
4-CF_3SO_2-Aniline	473-27-8	33.11	21.8[7]			1400
2,3,4,5,6-Cl_5-Aniline	527-20-8	32.79				1415
Indole	120-72-9	32.78	20.95[3]	16.97[20]	1431[21]; 1440[22]	1441
2-NO_2-Aniline	88-74-4	32.63		17.7[23]		1436
N-Me-4-NO_2-Aniline	100-15-2	32.62		18.2[23]		1488
4-NO_2-Aniline	100-01-6	32.58	20.9[7]	18.2[23]	1407[24]	1421
(2-NO_2-C_6H_4)(Ph)NH[g]	119-75-5	31.79	19.2[d] (17.7[25])	18.0[23]		1421
2-MeO-Carbazole	6933-49-9	31.78				1417
Carbazole	86-74-8	31.74	19.9[3]	16.7[26]	1412[21]	1420
2-NH_2-4-NO_2-Aniline	99-56-9	31.75				1416
3-Cl-4-NO_2-Aniline	825-41-2	31.53				1403
4-Cl-2-NO_2-Aniline	89-63-4	31.06	18.9[3]	17.1[19]		1412
5-Cl-2-NO_2-Aniline	1635-61-6	31.03				1411
1,3-Ph_2-Urea	102-07-8	30.96	19.6[3]			1396
(2-NO_2-C_6H_4)(4-Cl-C_6H_4)NH	23008-56-2	30.92				1402
2-Cl-6-NO_2-Aniline	769-11-9	30.84				1423
7-Azaindole	271-63-6	30.79		12.1[27,f]		1437
4-Azaindole[e]	272-49-1	30.49		15.5[28e]; 16.1[28e]		1422
2-Cl-4-NO_2-Aniline	121-87-9	30.38		18.06[29]		1398
Benzo[c]carbazole	205-25-4	30.33				1401
3-MeCOO-Indole	608-08-2	30.2				1427
Benzo[a]carbazole	239-01-0	30.20				1400
7-NO_2-Indole	6960-42-5	30.12				1415
4-NH_2-C_5F_4N	1682-20-8	30.12	18.7[d] (19.2[30])		1392[31]	1407
5-Azaindole	271-34-1	30.06				1414
Indolo[2,3-*a*]carbazole	60511-85-5	29.9				1387
(5-Cl-2-NO_2-C_6H_3)(Ph)NH	25781-92-4	29.88				1397
Indazole	271-44-3	29.79	18.2[26]	13.86[26]	1425[32]	1433
6-Azaindole	271-29-4	29.75				1413
2,3-Cl_2-6-NO_2-Aniline	65078-77-5	29.43				1403
Norharman	244-63-3	29.33		14.53[33]		1398
2,4-Cl_2-6-NO_2-Aniline	2683-43-4	29.26		16.39[29]		1401
2,5-Cl_2-4-NO_2-Aniline	6627-34-5	29.20	17.4[7]	16.05[34]		1380

(4-NO_2-C_6H_4)(Ph)NH[g]	836-30-6	28.87	16.85[7]	15.6[23]	1374[31g]	1384
4-NO_2-1-Naphthalenamine	776-34-1	28.85	17.4[d] (18.0[35])			1385
2,6-Cl_2-4-NO_2-aniline	99-30-9	28.30		15.55[34]		1387
Benzimidazole	51-17-2	27.92	16.4[3]	12.86[36]		1403
2,4-$(NO_2)_2$-Aniline	97-02-9	27.64	15.9[7]	15.0[34]		1367
Benzotriazole	95-14-7	22.98	11.92[3]	8.57[37]	1384[32]	1383

[a] pK_a values from this work (Table 1). [b] Experimental GA values. [c] Computational GA values (this work). [d] Original values from the respective publications (shown in parentheses) were corrected in ref 38. [e] In the abstract and the main text of ref 28 two different pK_a(H_2O) values were presented for 4-azaindole and it was not possible to tell which one is the correct one. [f] Highly doubtful value. [g] The GA value of 1374 kJ mol^{-1}, actually belonging to (4-NO_2-C_6H_4)(Ph)NH, is erroneously assigned to (2-NO_2-C_6H_4)(Ph)NH in the NIST Webbook.

Table 3. pK_a(MeCN) values predicted using conversion equations (eq 6 and eq 7).[a]

Compound	**pK_a(MeCN)[d]**	**Prediction from pK_a(DMSO)**			
		NH[b]	**Difference**	**All[c]**	**Difference**
2,3,5,6-Cl_4-Aniline	33.51	33.30	-0.21	33.09	-0.42
4-CF_3SO_2-Aniline	33.11	34.10	0.99	33.94	0.83
4-NO_2-Aniline	32.58	32.90	0.32	32.98	0.40
(2-NO_2-C_6H_4)(Ph)NH	31.79	31.20	-0.59	31.49	-0.30
Carbazole	31.74	32.20	0.46	32.23	0.49
4-Cl-2-NO_2-Aniline	31.06	30.90	-0.16	30.85	-0.21
1,3-Ph_2-Urea	30.96	31.60	0.64	30.74	-0.22
4-NH_2-C_5F_4N	30.12	30.70	0.58	30.64	0.52
Indazole	29.79	30.20	0.41	30.43	0.64
2,5-Cl_2-4-NO_2-Aniline	29.20	29.40	0.20	29.26	0.06
(4-NO_2-C_6H_4)(Ph)NH	28.87	28.85	-0.02	28.99	0.12
4-NO_2-1-Naphthalenamine	28.85	29.40	0.55	29.26	0.41
Benzimidazole	27.92	28.40	0.48	28.51	0.59
2,4-$(NO_2)_2$-Aniline	27.64	27.60	-0.04	27.66	0.02
Benzotriazole	22.98	23.62	0.64	23.74	0.76
		RMSE[e]	**0.49**		**0.46**

[a] Conversion equations taken from ref 6. [b]pK_a(MeCN) values predicted from pK_a(DMSO) using equation 6. [c]pK_a(MeCN) values predicted from pK_a(DMSO) using equation 7 [d]Experimental values from this work. [e]Root mean square error.