

**Table 2. Continuous Self-consistent Basicity Scale of Neutral Bases in THF Solution<sup>a</sup>**

Compound	$pK_{ip}(\text{THF})^c$ $pK_a(\text{THF})^c$	
EtP <sub>1</sub> (pyrr)		21.4 21.5
4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>2</sub> (pyrr)	0.65 <sup>b</sup>	20.8 21.3
H <sub>2</sub> NP <sub>1</sub> (pyrr)	0.78 <sup>b</sup> 1.34 <sup>b</sup>	20.7 20.8
PhP <sub>2</sub> (pyrr)	1.50 <sup>b</sup> 0.40 <sup>b</sup> 1.64 <sup>b</sup>	20.1 20.5
<i>t</i> -BuP <sub>1</sub> (pyrr)	1.60 <sup>b</sup> 0.17 <sup>b</sup> 2.52 <sup>b</sup> 0.40 <sup>b</sup> 0.54 <sup>b</sup> 1.05 <sup>b</sup>	20.1 20.2
TBD	0.88 <sup>b</sup> 1.28 <sup>b</sup>	19.7 19.4
PhP <sub>2</sub> (dma)	0.6	19.3 19.6
<i>t</i> -BuP <sub>1</sub> (dma)	1.5	18.8 18.8
DBU	1.6	17.8 16.6
4-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	0.83	17.1 17.1
TMG	0.2 1.1 1.3	16.9 15.3
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>2</sub> (pyrr)	0.53 0.55 0.97 0.2	16.7 17.3
4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	0.62	16.6 16.6
PhP <sub>1</sub> (pyrr)	0.64	15.9 15.9
4-Br-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)		15.3 15.3
Pyrrolidine	0.05 0.42 0.03	15.3 13.5
PhP <sub>1</sub> (dma)	1.70 0.3 1.25 0.29	15.3 15.3
PhTMG	1.0 0.98 0.95 0.47 1.61	15.0 14.0
4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)		14.6 14.6
1-NaphP <sub>1</sub> (pyrr)	0.14 0.91 1.36	14.2 14.2
Et <sub>3</sub> N	1.07 0.8 0.25 1.58 1.61	14.1 12.5
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	1.3 0.54	13.2 13.2
4-Me <sub>2</sub> N-Pyridine	1.2 0.7	13.0 11.2
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (dma)		12.5 12.5
2,5-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.05	11.9 11.9
2,6-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.16 1.1 1.05	11.8 11.8
DMAN	0.87 1.54	11.7 11.1
4-Cl-2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)		10.8 10.8
5-Cl-2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.45 1.2	10.1 10.1
2,4,6-Me <sub>3</sub> -Pyridine	0.97 0.55	9.6 8.1
2-NO <sub>2</sub> -4-CF <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.45 0.79	9.6 9.6
4-MeO-Pyridine	0.31 1.01	9.1 7.3
2,6-Me <sub>2</sub> -Pyridine	0.45 0.71	8.8 7.2
4-MeO-Aniline	0.24 0.32 0.71	8.3 6.5
2-Me-Pyridine	0.32 0.07	8.1 6.3
2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.57 0.29 0.07	8.0 8.0
2,6-Cl <sub>2</sub> -4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub> P <sub>1</sub> (pyrr)	0.71 0.30	7.8 7.8
2,6-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	0.13	7.5 7.5
Pyridine	0.34 0.49	7.4 5.5
Aniline	0.43	7.0 5.2
2-Me-Aniline	0.46 0.52	6.9 5.1
N,N-Me <sub>2</sub> -Aniline	1.10	6.5 4.9
4-Br-Aniline	2.1	5.8 4.0
2-MeO-Pyridine	1.40	4.4 2.6

<sup>a</sup> The numbers on the arrows are the direct experimental  $\Delta pK_{ip}$  values (uncorrected for ion pairing) obtained from UV-Vis spectrophotometric measurements if not indicated otherwise. <sup>b</sup> NMR measurements. <sup>c</sup> Absolute  $pK_{ip}(\text{THF})$  and  $pK_a(\text{THF})$  estimated values for conjugate acids of the respective bases.

**Table 4. Basicity Data of the Bases in AN, H<sub>2</sub>O, and the Gas Phase**

base	p <i>K</i> <sub>a</sub> values in AN <sup>a</sup>	GB (kcal/mol) <sup>b</sup>	p <i>K</i> <sub>a</sub> values in H <sub>2</sub> O <sup>c</sup>
EtP <sub>1</sub> (pyrr)	28.89 <sup>d</sup>		
<i>t</i> -BuP <sub>1</sub> (pyrr)	28.35 <sup>d</sup>		
PhP <sub>2</sub> (dma)	26.28		
TBD	25.96 <sup>e</sup>	244.3	
<i>t</i> -BuP <sub>1</sub> (dma)	26.88 <sup>d</sup>		
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>2</sub> (pyrr)	25.24		
4-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	23.71		
DBU	24.16	239.6	
4-MeO-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	22.95		
PhP <sub>1</sub> (pyrr)	22.17		
4-Br-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	21.05		
TMG	23.3 <sup>f</sup>	238.4	13.6
PhP <sub>1</sub> (dma)	21.07		
4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	19.93		
1-NaphtP <sub>1</sub> (pyrr)	20.42		
PhTMG	20.63	236.9	12.18 <sup>g</sup>
pyrrolidine	19.34	218.8	11.1
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (pyrr)	19.97		
2-Cl-C <sub>6</sub> H <sub>4</sub> P <sub>1</sub> (dma)	18.87		
Et <sub>3</sub> N	18.63	227	10.7
2,5-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	18.32		
2,6-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	18.36		
DMAP	17.75	232.1	9.53
DMAN	18.42	238.0	12.1 <sup>h</sup>
4-Cl-2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	17.48		
5-Cl-2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	17.07		
2-NO <sub>2</sub> -4-CF <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	16.33		
2,4,6-Me <sub>3</sub> -pyridine	14.78		
2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	14.68		
2,6-Cl <sub>2</sub> -4-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub> P <sub>1</sub> (pyrr)	14.25		
2,6-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> P <sub>1</sub> (pyrr)	13.91		
4-MeO-pyridine	14.04	222.2	6.5
2,6-Me <sub>2</sub> -pyridine	13.92	222.5	6.70
4-MeO-aniline	11.66	207.6	5.3
2-Me-pyridine	13.11	219.2	5.94
pyridine	12.33 <sup>i</sup>	214.7	5.25
aniline	10.42	203.3	4.6
2-Me-aniline			4.4
<i>N,N</i> -Me <sub>2</sub> -aniline	11.23	217.3	5.1
4-Br-aniline	9.25		3.9
2-MeO-pyridine			3.1

<sup>a</sup> Slightly revised p*K*<sub>a</sub> values of conjugate acids of corresponding bases obtained in previous work (ref 14) or in this work if not noted otherwise. <sup>b</sup> Gas-phase basicities from ref 25. <sup>c</sup> p*K*<sub>a</sub> values of conjugate acids of corresponding bases from refs 24 or 23 if not noted otherwise. <sup>d</sup> Reference 17. <sup>e</sup> Reference 26. <sup>f</sup> Reference 27. <sup>g</sup> Reference 28. <sup>h</sup> Reference 29. <sup>i</sup> Anchor of AN scale; value taken from ref 22.