TABLE 1. Observed pK_a Values for 3,7-Diazabicyclo[3.3.1]nonanes, Determined as pK_{BH^+} for the Conjugated Acid, Spectrophotometrically in AN Solution

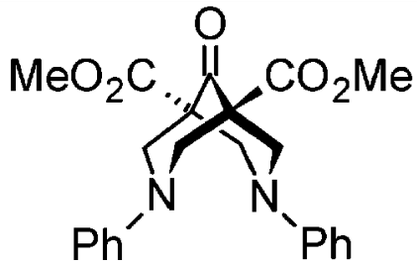
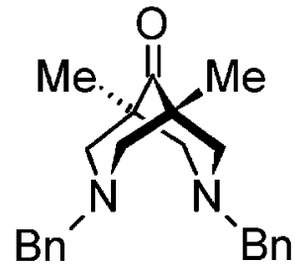
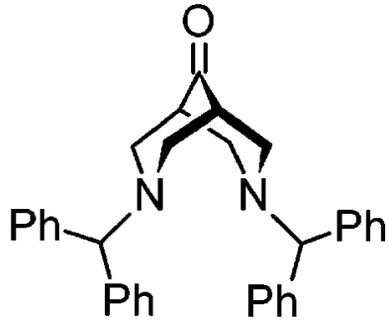
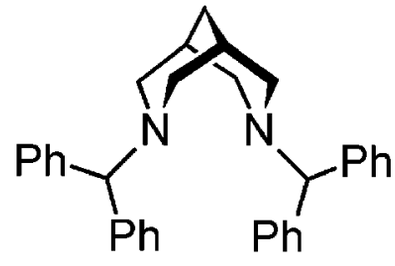
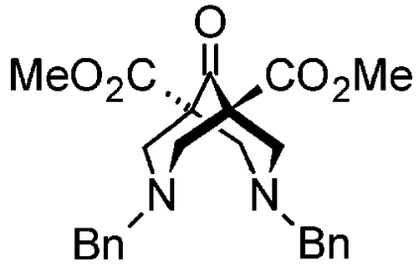
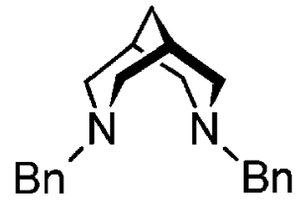
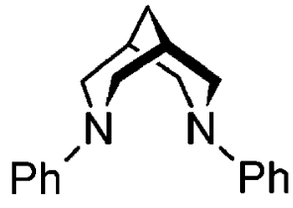
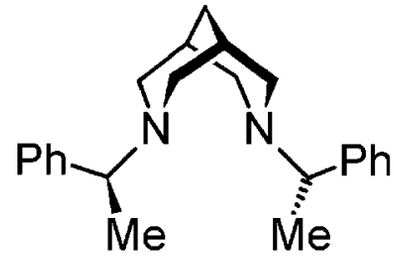
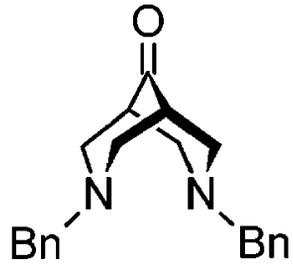
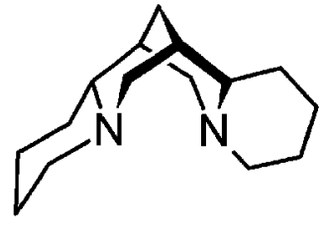
Bispidine	Structure	pK_a	Bispidine	Structure	pK_a
1		8.13	**6**		17.48
2		13.48	**7**		17.79
3		13.81	**8**		21.25
4		13.97	**9**		21.38
5		16.93	**10**		21.66

TABLE 6. Results of UV−Vis Spectrophotometric Titration Experiments in AN Solution and Assigned p$K_{a,AN}$ Values for the Conjugate Acid Forms of the Compounds 1−10

	reference base		concn,[b] 10^5 M						
bispidine	identity	pK_a[a]	bispidine	reference base	acid[c] used	calcn method[d]	ΔpK_a[e]	*s*	assigned pK_a value
1	3-NO_2-aniline	7.68	1.59	4.74	T	S	0.44	0.05	8.13
	3-NO_2-4-F-aniline	7.67	2.56	5.67	T	S	0.42	0.04	
	2,6-$(MeO)_2$-pyridine	7.64	2.49	7.11	T	S	0.48	0.07	
	2,4-F_2-aniline	8.39	2.58	8.33	T	S	−0.23	0.03	
	2-Cl-pyridine	6.79	3.29	13.25	T	S	1.38	0.05	
2	2,6-Cl_2-4-NO_2-C_6H_2-P_1(pyrr)	14.43	1.73	3.67	M	NV/S	−0.95	0.1	13.48
	2,6-$(NO_2)_2$-C_6H_3-P_1(pyrr)	14.12	1.50	5.22	M	NV/S	0.65	0.05	
3	2,4-$(NO_2)_2$-C_6H_3-P_1(pyrr)	14.88	3.57	3.19	M	NV/S	−0.95	0.1	13.81
	2,6-$(NO_2)_2$-C_6H_3-P_1(pyrr)	14.12	2.78	7.53	M	NV	−0.35	0.05	
	2,6-Cl_2-4-NO_2-C_6H_2-P_1(pyrr)	14.43	2.74	4.03	M	NV	−0.62	0.05	
	3-NH_2-pyridine	14.17	1.67	6.63	M	NV/S	−0.44	0.1	
4	2,4-$(NO_2)_2$-C_6H_3-P_1(pyrr)	14.88	2.31	3.07	M	S	−0.90	0.03	13.97
	2,6-$(NO_2)_2$-C_6H_3-P_1(pyrr)	14.12	1.91	2.91	M	S	−0.17	0.01	
	2,6-Cl_2-4-NO_2-C_6H_2-P_1(pyrr)	14.43	2.50	3.68	M	S	−0.47	0.01	
5	2-NO_2-4-CF_3-C_6H_3-P_1(pyrr)	16.54	2.45	1.78	M	NV	0.39	0.05	16.93
	2-NO_2-5-Cl-C_6H_3-P_1(pyrr)	17.27	3.00	2.08	M	NV	−0.34	0.05	
	2-NO_2-4-Cl-C_6H_3-P_1(pyrr)	17.68	2.66	2.83	M	NV	−0.76	0.05	
6	2-NO_2-4-CF_3-C_6H_3-P_1(pyrr)	16.53	1.98	3.61	M	NV	0.96	0.05	17.48
	2-NO_2-5-Cl-C_6H_3-P_1(pyrr)	17.27	4.16	1.85	M	NV/S	0.19	0.07	
	4-NMe_2-pyridine	17.95	1.43	4.50	M	NV/S	−0.47	0.1	
	4-NMe_2-pyridine	17.95	2.67	5.02	T	NV/S	−0.46	0.1	
	2-NO_2-4-Cl-C_6H_3-P_1(pyrr)	17.68	1.88	3.87	M	NV/S	−0.19	0.1	
7	2,5-Cl_2-C_6H_3-P_1(pyrr)	18.52	1.13	1.86	M	S	−0.70	0.04	17.79
	4-pyrrolidinylpyridine	18.33	1.04	3.23	M	NV/S	−0.59	0.1	
	4-NMe_2-pyridine	17.95	1.42	3.32	M	NV	−0.17	0.06	
	4-NO_2-C_6H_4-P_1(pyrr)	18.51	1.12	2.85	M	S	−0.70	0.06	
8	PhP_1(dma)	21.25	1.24	2.49	M	NV	0.03	0.06	21.25
	4-Br-C_6H_4-P_1(pyrr)	21.19	1.84	1.14	M	NV/S	0.08	0.06	
	PhP_1(dma)Me	21.03	1.14	2.04	M	NV/S	0.23	0.1	
	4-CF_3-C_6H_4-P_1(pyrr)	20.16	1.49	1.61	M	NV/S	1.01	0.1	
	PhTMG	20.84	1.54	2.71	M	NV	0.43	0.06	
9	2-Cl-C_6H_4-P_1(pyrr)	20.17	2.34	2.74	M	NV/S	1.2	0.1	21.38
	PhP_1(dma)	21.25	1.79	3.62	M	NV/S	0.11	0.05	
	4-Br-C_6H_4-P_1(pyrr)	21.19	1.79	2.99	M	NV/S	0.21	0.05	
	$PhP_1(dma)_2Me$	21.03	2.17	2.67	M	NV	0.36	0.05	
	PhTMG	20.84	2.05	3.40	M	NV/S	0.52	0.1	
10	PhP_1(pyrr)	22.34	4.39	3.87	M	NV/S	−0.63	0.1	21.66
	PhP_1(dma)	21.25	4.07	3.17	M	NV/S	0.41	0.05	
	PhP_1(dma)	21.25	6.45	3.53	T	NV/S	0.42	0.05	
	4-Br-C_6H_4-P_1(pyrr)	21.19	3.58	3.14	M	NV/S	0.49	0.1	
	$PhP_1(dma)_2Me$	21.03	4.11	2.67	M	NV/S	0.60	0.07	
	PhTMG	20.84	3.97	4.32	M	NV/S	0.77	0.07	

[a] Reference 44. [b] Concentration of bispidine and reference base in mixture. [c] Abbreviation of the acid titrated with: M = CH_3SO_3H, T = CF_3SO_3H. [d] Calculation method: NV, bispidine as "nonvisible", ΔpK_a calculated on molar basis; S, calculated from UV−vis spectra. [e] ΔpK_a = pK_a(bispidine) − pK_a(reference base).