83. On the Basicity of Triarylmethylamines in Solution

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Summary

The pK_a^* of 11 triarylmethylamines (tritylamines), eight of which are new, and some related bases were measured in methylcellosolve/water 80:20 (MCS); some were also measured in dioxane/water 60:40 (Dx), acetonitrile (An), nitrobenzene (Nb) and acetic acid (Ac). 1) The influence of the aryl groups on the basicity is essentially additive; 2) In different solvents, similar linear free energy relationships were found, with differences in ρ^* characteristic of solvation; 3) The influence on basicity of substituents of the aryl groups follows *Hammett*'s relationship. These results indicate a preponderance of inductive effects. *N,N*-Dimethyltritylamine (**3b**) ($pK_a^{MCS} = 3.40$) shows a marked crowding effect, absent in the isomeric tertiary amines **13** and **14**. Tri-*p*-nitrotritylamine (**10a**) ($pK_a^{MCS} = 3.10$), *N,N*-dimethyl-tri-*p*-nitrotritylamine (**10b**) ($pK_a^{Ac} = 0.50$), and **3b** are particularly weak bases; the base-weakening effect of the trinitrotrityl group is similar to that of the cyanomethyl and trifluoroethyl groups.

The measurements of proton affinities of organic compounds in the gas phase have put the understanding of acidity and basicity in solution on a new basis [1]. The basicity of aliphatic amines is (partly) determined by the inductive effects of the groups bound to nitrogen [1] [2]; this has been expressed by *Hall*'s linear free energy relationship between pK_a values and *Taft*'s polar substituent constants σ^* [3], or between proton affinities in the gas phase and *Taft*'s inductive substituent constants σ_I [1] [4]. Solvation effects, and particularly the number of hydrogen bonds formed between the ammonium ion and a protic solvent, are a second important factor [1–3] [5]; (protic) solvents attenuate the inductive effects by partly taking over from the polarizable substituents the role of stabilizing the positive charge [1] [6].

Steric effects are generally less important [1] [3] [7]; in cases of heavy crowding, however, as in 2,6-di-*t*-butyl-substituted aromatic bases (pyridines, anilines, dimethylanilines, phenoxide ions), significant base-weakening steric effects have been observed [8], but only in solution [1][2]). Triphenylmethyl is another sterically highly

[1]) Taken from the Doctoral Thesis of *J.-C. Farine*, Lausanne 1968.

[2]) In the gas phase only kinetic effects upon H^+-transfer have been observed (see [1], p. 87).

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demanding group; starting from the qualitative observation that triphenylmethylamine (tritylamine) is a comparatively weak base in solution, we investigated some primary and tertiary triarylmethylamines to see whether, apart from the general inductive effects, steric effects can be found in solution. The series includes some compounds *p*-substituted in one or several aryl groups, in order to determine the transmission of purely inductive effects (see *Table*).

Most of the compounds were prepared by reaction of the corresponding arylmethyl halides with ammonia in benzene [9] [10] or dimethylamine in acetonitrile [11]. The *p*-hydroxyphenyl compound **7**, not directly accessible, was prepared by hydrolysis of the corresponding *p*-benzoyloxyphenyl derivative **8**; **10b** was obtained by *N*-methylation of **10a**.

The basicity of the compounds **2–14** was determined by potentiometric titration. As most of the bases were not sufficiently soluble in water, the solvents chosen were methylcellosolve/water 80:20 (MCS) proposed as a standard solvent system [12], and for comparison, the similar system dioxane/water 60:40 (Dx) [13]. Some measurements in aprotic solvents were also made, choosing acetonitrile (An) [14–16] and nitrobenzene (Nb) [16] [17] of similar polarity. The weakest bases, **3b**, **10a**, **10b**, were measured in acetic acid (Ac) [18]. The *Table* includes some literature values. Each pK_a system has been adapted to literature values by measuring known standards.

Table. *Apparent pK_a-values of arylalkylamines at 25° ± 0.1° in methylcellosolve/water 80:20 (MCS), dioxane/water 60:40 (Dx), acetonitrile (An), nitrobenzene (Nb), and acetic acid (Ac)*

No	R^1	R^2	R^3	$\Sigma\sigma^{*a)}$	pK_a^{MCS}	pK_a^{Dx}	pK_a^{An}	pK_a^{Nb}	pK_a^{Ac}
$R^1R^2R^3CNH_2$									
	H	H	H	0.98	9.94 [12]		18.37 [15]	6.85 [17]	
1a	Ph	H	H	1.19	8.62 [12]	8.82	16.76 [15]	6.00	
2a	Ph	Ph	H	1.39	7.17	7.30	14.91	4.15	
3a	Ph	Ph	Ph	1.54	6.10	6.20	13.40	2.50	
4	*p*-Me–C_6H_4	Ph	Ph		6.23	6.37		2.69	
5	(*p*-Me–C_6H_4)$_3$				6.51	6.57		3.35	
6	*p*-MeO–C_6H_4	Ph	Ph		6.32	6.40		2.80	
7	*p*-HO–C_6H_4	Ph	Ph		6.47	6.64			
8	*p*-PhCOO–C_6H_4	Ph	Ph		5.85	5.90			
9	*p*-NO_2–C_6H_4	Ph	Ph		5.05	5.25		1.40	
10a	(*p*-NO_2–C_6H_4)$_3$				3.10	3.25	9.40	– 1.40	1.98
11	α-$C_{10}H_7$	Ph	Ph	1.68	5.30	5.42		1.99	
12	α-$C_{10}H_7$	H	H	1.25	7.75[b)]				
$R^1R^2R^3CNMe_2$									
	H	H	H	0.00	8.31 [12]		17.61 [15]	6.95 [17]	
1b	Ph	H	H	0.21	7.45 [19]				
2b	Ph	Ph	H	0.41	5.99 [19]				
3b	Ph	Ph	Ph	0.56	3.40				2.62
10b	(*p*-NO_2–C_6H_4)$_3$								0.50
13	Ph_2CH–N(Me)–CH_2Ph			0.62	4.76[b)]				
14	$(PhCH_2)_3N$			0.63	4.00[b)]				

[a)] See footnote 4.
[b)] Measured by Prof. *W. Simon*, ETH Zürich.

Discussion. – In the series methylamine, benzylamine (**1a**), benzylhydrylamine (**2a**), tritylamine (**3a**) the decrease in basicity in MCS is regular: 1.3, 1.4, and 1.1 pK^* units per added phenyl group. The additivity points to a purely inductive effect. It can be expressed by a free energy relationship between pK_a^{MCS} and *Taft*'s polar substituent constants σ^* [20] [21][3]). The straight line correlating the points *(Fig.)* has a slope of $\rho^* = 6.6 \pm 0.3$ (r = 0.995, in MCS)[4]). In aqueous dioxane (Dx), a solvent similar to MCS, we found $\rho^* = 7.0 \pm 0.3$ (r = 0.998), in the aprotic systems An $\rho^* = 8.9 \pm 0.4$ (r = 0.998) and Nb $\rho^* = 7.5 \pm 0.7$ (r = 0.987). These values are much

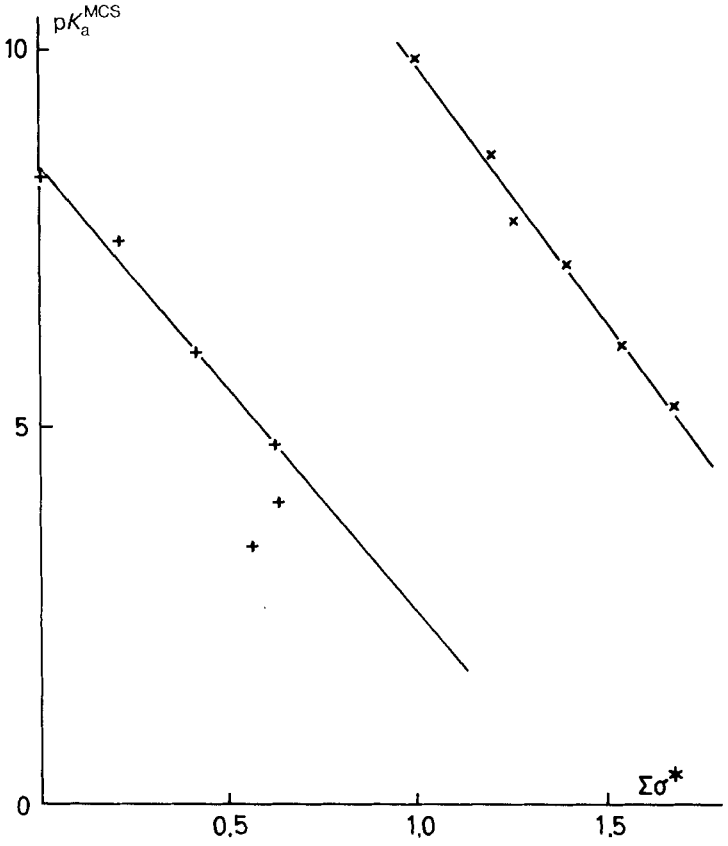

Figure.
pK_a^{MCS} values of primary (×) and tertiary (+) benzyl-type amines in function of $\Sigma\sigma^*$

[3]) We prefer here the σ^*-scale [20] to the σ_I-scale [22] [7] because of its well established additivity [20] [23], particularly for amine basicity [2] [3]. For the groups relevant for this work (R = Me, $PhCH_2$, Ph_2CH, Ph_3C) σ_I-values based upon reactivity measurements [24] fit well the proportionality with σ^* [20] [22][4]): $\sigma_I = 0.45\ \sigma^*$. On the other hand σ_I-values based as usual [7] upon pK_a of substituted acetic acids would fail here, as a consequence of their solvent dependence; indeed for our R-groups the pK_a^{MCS}-values of RCOOH show no significant differences (6.84, 6.73, 6.76, and 6.96 [24]).

[4]) The following group values were used: H = 0.49; Me = 0.00; $PhCH_2 = 0.21$; $Ph_2CH = 0.41$ [20]; $Ph_3C = 0.56$ [21]; α-$C_{10}H_7CH_2 = 0.27$ was estimated from σ_I (obtained from reactivity [21] and acidity [7] measurements) and the conversion factor 0.45; α-$C_{10}H_7$-$CPh_2 = 0.7$ was evaluated using $\sigma^* = 0.21$ for each additional sp^3-bound Ph [20].

higher than that found by *Hall* [3] for aqueous solution ($\rho^* = 3.14$). This difference can be ascribed to the change of solvent; in other series, ρ increases in passing from water to less polar aqueous solvent mixtures (or less polar solvents), for instance for the dissociation of benzoic acids: $\rho = 1.00$ (water), 1.57 (50% ethanol [23]), 1.66 (MCS [25]), 2.15 (benzene [23]). In the gas phase the increase of ρ (expressed as the 'attenuation factor' of water compared with the gas phase in $\sigma_I/\delta\Delta G°$ plots) is even more important [1] [26].

The tertiary amines give a similar general picture of decrease of basicity with increasing number of phenyl groups: Me_3N, **1b** and **2b** fit reasonably well a straight line of $\rho^* = 5.9 \pm 0.4$ (r = 0.995, in MCS), *i.e.* similar to the value found for primary amines, but much higher than *Hall*'s $\rho = 3.30$ [3] for simple tertiary amines in water *(Fig.)*. As before, we ascribe the higher ρ^* value to the change of solvent. Compound **3b** does not fit the straight line of $\rho^* = 5.9$, but is 1 pK unit weaker (see below). As **3b** is sterically crowded, we ascribe the decrease of basicity to steric hindrance to solvation of the conjugate acid. Until now such a steric effect upon basicity has been observed for 2,6-di-*t*-butyl-substituted aromatic bases (aniline, pyridine, phenolate) [8]; **3b** would be another structure exhibiting the same phenomenon.

In order to check the role of the special crowding effect in the low basicity of **3b**, it was compared with two isomeric tertiary amines, $PhCH_2{-}N(Me){-}CHPh_2$ (**13**) and $(PhCH_2)_3N$ (**14**). On the basis of inductive effects alone, the three compounds, all trimethylamines substituted by three phenyl groups, but on different C-atoms ($\Sigma\sigma^* = 0.60$, 0.61, and 0.62), should give similar pK_a^{MCS} values. However, significant differences were found: 3.40 (**3b**), 4.76 (**13**), and 4.00 (**14**). In the $pK_a^{MCS}/\Sigma\sigma^*$ plot *(Fig.)* the point of **13** is included in the correlation line and that of **14** not too far from it; **3b** shows the strongest deviation. *Newman* diagrams confirm that **13** and **14** can adopt less crowded conformations than **3b**.

The primary tritylammonium group did not show a steric effect comparable to the tertiary group. Even when one phenyl group in tritylamine **3a** was replaced by the sterically more demanding α-naphthyl group, the loss in basicity of 0.8 pK units (**3a**, $pK_a^{MCS} = 6.10$ and **11**, $pK_a^{MCS} = 5.30$) was not bigger than that found in going from benzylamine (**1a**, $pK_a^{MCS} = 8.62$) to α-naphthylmethylamine (**12**, $pK_a^{MCS} = 7.75$). The purely inductive character of this change is confirmed by the fit of **11** and **12** to the $\Delta pK_a/\sigma^*$ plot *(Fig.)*.

As mentioned above, the increase of the values of ρ^* may be due to change of solvent. Another interpretation might be steric hindrance to solvation, which would tend to improve the transmission of polar effects inside a molecule or the solvent cage [24] [27] and yield higher values of ρ^*. In this case the electronic effects of *p*-substituents in the aromatic ring should also be better transmitted, giving higher ρ in the *Hammett* plot. This has been observed, for instance, in comparing *Hammett* type ρ values for the basicity of substituted anilines (2.94) with the more hindered *N,N*-dimethylanilines (3.56) [28] [23], for the basicity of substituted benzylamines (1.06 [29]) and *N*-(2,4-dinitrophenyl)benzylamines (1.70 [30]), and for the acidity of substituted phenols (2.26) [23], 2,-dimethylphenols (2.70) [31] and 2,6-di-*t*-butyl-phenols (3.50) [27]. We would suppose that such an effect is absent from our compounds (with the exception of **3b**).

In order to test the transmission of polar effects in tritylamines, the basicity of the aryl substituted derivatives **4**–**10** were examined. As expected, *p*-substituents in the aryl groups, acting by their inductive effects only, follow *Hammett*'s relationship. It is significant that the action of three nitro groups on **3a** (**10a**, $\Delta pK^{MCS} = pK_x - pK_{3a} = -3.00$) is three times that of one nitro group (**9**, $\Delta pK^{MCS} = -1.05$); the same is true for methyl groups (3 Me (**5**): $\Delta pK^{MCS} = 0.41$; 1 Me (**4**): $\Delta pK^{MCS} = 0.13$). Plotting ΔpK_a^{MCS} of **3a**–**10a** against *Wepster*'s σ^n [32] gives a straight line with a slope $\rho^n = 1.32 \pm 0.04$ ($r = 0.998$)[5]). Substituted benzylamines $ArCH_2NH_2$ show $\rho = 1.05$ (in water) [29]; the small difference in ρ can again be ascribed to the change of solvent.

The sensitivity of pK_a to polar substituent effects should increase with decreasing ion-solvating power of the solvent; the explanation is that the less the ions are stabilized by solvation, the better the inductive effects are propagated in their interior [24] [27] [34]. In nitrobenzene we found $\rho^n = 1.72 \pm 0.06$ ($r = 0.997$), whereas in aqueous dioxane (60:40) of solvating power similar to that of aqueous methylcellosolve $\rho^n = 1.29 \pm 0.05$ ($r = 0.997$), thus confirming the inductive character [16] and the absence of steric effects.

With a base-weakening inductive effect of 6.8 units (in MCS, compared with $MeNH_2$) the trinitrotrityl group is a strong electron-attractor. In this respect it is of the same order of magnitude as the cyanomethyl group [35] and the 2,2,2-trifluoroethyl group [36], which show base-weakening effects of 5.3 and 5.0 pK-units respectively (in water).

Combining the inductive effect of the trinitrotrityl group with the special crowding present in dimethyltritylamine **10a**, we obtain a particularly weak base **10b**. For solubility reasons it was not possible to measure its basicity in MCS or Dx; we therefore used anhydrous acetic acid (Ac), where indeed **10b** showed the expected effect: $pK_a^{Ac} = 0.50$[6]).

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Experimental Part

General remarks. See [37]. Microanalyses: Dr. *K. Eder*, Geneva.

Syntheses. *Known compounds:* **3a** [38], **11** [39], **2b** [40], **13** [41].

Preparation of triarylmethylamines [10]. – Dry ammonia was bubbled into a solution of 5 to 10 g of the triarylmethyl halide (chloride or bromide) in a tenfold volume of benzene. After 6 h, the precipitate (NH_4Cl, or NH_4Br) was filtered off and the solvent was evaporated. The residue was dissolved in dry ether and the solution was saturated with dry HCl. The precipitated amine hydrochloride was washed with ether, dried, and then treated with 20% NaOH. The amine could either be filtered off and recrystallized, or extracted with ether and isolated in the usual way.

Triphenylmethylamine (**3a**) [10]. Yield 77%; m.p. 105° (from ether). – IR. ($CHCl_3$): 3385, 3320 cm^{-1} (NH_2). – ^{1}H-NMR. (CCl_4): 2.09 (*s*, 2 H, NH_2); 7.35 (*m*, 15 H, 3 Ph).

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[5]) Use of *Hammett*'s σ [33] would give $\rho = 1.23 \pm 0.06$ ($r = 0.997$).

[6]) With the exception of **10b**, **3b** ($pK_a^{Ac} = 2.62$) and **10a** ($pK_a^{Ac} = 1.98$) the bases were not weak enough for titration in the anhydrous acetic acid/$HClO_4$ system (Ac) [18].

*Diphenyl-*p*-tolylmethylamine* (**4**). From the corresponding chloride [42], yield 50%, m.p. 77° (from ether). – IR. ($CHCl_3$): 3383, 3320 (NH_2), 2950 cm^{-1} (CH_3).

$C_{20}H_{19}N$ (273.4) Calc. C 87.89 H 7.02 N 5.13% Found C 87.87 H 6.93 N 5.24%

N-*Acetyl derivative:* m.p. 217° (from EtOH/H_2O). – IR. ($CHCl_3$): 3455, 1685 cm^{-1} (amide).

$C_{22}H_{21}NO$ (315.4) Calc. C 83.77 H 6.72 N 4.45% Found C 83.11 H 6.82 N 4.44%

*Tri-*p*-tolylmethylamine* (**5**) [9]. Yield 65%, m.p. 112° ([9] m.p. 112°). – IR. ($CHCl_3$): 3382, 3320 cm^{-1} (NH_2).

*Diphenyl-*p*-methoxyphenylmethylamine* (**6**). From the corresponding chloride [43], yield 70%, m.p. 43° (from ether/petroleum ether). – IR. ($CHCl_3$): 3382, 3320 (NH_2); 2850 cm^{-1} (OCH_3).

$C_{20}H_{19}NO$ (289.4) Calc. C 83.00 H 6.62 N 4.48% Found C 83.04 H 6.68 N 4.88%

N-*Tosyl derivative,* prepared with tosyl chloride in pyridine at reflux temperature, m.p. 191° (from EtOH/H_2O). – IR. ($CHCl_3$): 3402, 1610 (tosylamide); 2850 cm^{-1} (OCH_3).

$C_{27}H_{25}NO_3S$	Calc.	C 73.08	H 5.68	N 3.15	S 7.23%
(443.6)	Found	„ 73.01	„ 5.58	„ 3.29	„ 7.00%

*Diphenyl-*p*-benzoyloxyphenylmethylamine* (**8**). From the corresponding chloride [44], yield 75%, m.p. 122–123° (from benzene/petroleum ether). – IR. ($CHCl_3$): 3385, 3320 (NH_2); 1745 cm^{-1} (ester).

$C_{26}H_{21}NO_2$ (391.5) Calc. C 82.30 H 5.85 N 3.69% Found C 82.33 H 5.51 N 3.80%

N-Acetyl derivative. M.p. 202° (from EtOH/H_2O). – IR. ($CHCl_3$): 3450, 1688 (amide); 1740 cm^{-1} (ester).

$C_{28}H_{23}NO_3$ (421.5) Calc. C 79.79 H 5.49 N 3.32% Found C 79.42 H 5.59 N 3.32%

*Diphenyl-*p*-nitrophenylmethylamine* (**9**). From the corresponding bromide [45], yield 70%, m.p. 121–122° (from ether/petroleum ether). – IR. ($CHCl_3$): 3390, 3320 (NH_2); 1595, 1352 cm^{-1} (NO_2). – ^{1}H-NMR. (CCl_4): 2.17 (*s*, 2 H).

$C_{19}H_{16}N_2O_2$ (304.3) Calc. C 74.07 H 5.30 N 9.21% Found C 74.07 H 5.47 N 9.05%

N-*Acetyl derivative:* m.p. 201° (from EtOH). – IR. ($CHCl_3$): 3455, 1695 (amide); 1510, 1352 cm^{-1} (NO_2).

$C_{21}H_{18}N_2O_3$ (346.4) Calc. C 72.81 H 5.24 N 8.11% Found C 72.77 H 5.10 N 8.18%

*Tris(*p*-nitrophenyl)methylamine* (**10a**). A mixture of 10 g tri(*p*-nitrophenyl)methylbromide [42] with liquid ammonia was heated for 7 h in an autoclave to 80°/50 atm. After cooling to RT., the excess ammonia was evaporated; ether was added and NH_4Br was filtered off. The solution was saturated with HCl and **10a** · HCl was filtered off and washed with ether. The amine **10a** was isolated by treating with 2N NaOH and extraction with ether; it was recrystallized from $CHCl_3$/petroleum ether: 2.5 g (30%), m.p. 198°. – IR. (CH_2Cl_2): 3390, 3320 (NH_2); 1528, 1350 cm^{-1} (NO_2).

$C_{19}H_{14}N_4O_6$ (394.4) Calc. C 57.87 H 3.58 N 14.21% Found C 58.01 H 3.66 N 14.21%

N-*Acetyl derivative:* m.p. 282–284° (from EtOH). – IR. ($CHCl_3$): 3440, 1690 (amide); 1522, 1350 cm^{-1} (NO_2).

$C_{21}H_{16}N_4O_7$ (436.4) Calc. C 57.81 H 3.71 N 12.85% Found C 57.69 H 3.67 N 12.92%

*Diphenyl-*p*-hydroxyphenylmethylamine* (**7**). A mixture of 2 g of the benzoyloxyamine **8** and 2 g of NaOH in 50 ml EtOH were left at RT. After the solution became homogeneous, 200 ml of H_2O were added and the mixture was neutralized with dilute hydrochloric acid. The mixture was extracted with ether and the extract was washed with water, dried, and the ether evaporated. The residue was crystallized several times from ether/petroleum ether; yield 70%; m.p. 123–124°. – IR. ($CHCl_3$): 3310 (NH_2); 3605 cm^{-1} (OH).

$C_{19}H_{17}NO$ (275.3) Calc. C 82.88 H 6.23 N 5.09% Found C 82.71 H 6.40 N 4.76%

N,N-*Dimethyltriphenylmethylamine* (**3b**) [11]. A solution of 2 g (6 mmol) of trityl bromide in 20 ml acetonitrile was saturated during 2 h at RT. with gaseous dimethylamine, then left a further 2 h at RT. Petroleum ether was added in order to precipitate Me_2NH_2Br, which was removed by filtration. The solvent was evaporated from the filtrate and the residue recrystallized from ethanol: 1.5 g (85%) of **3b**, m.p. 93–95° ([11] m.p. 94°). – IR. ($CHCl_3$): 2875, 2840, 2820, 2800 cm^{-1} ($NHCH_3$).

N,N-*Dimethyl-tris(*p-*nitrophenyl)methylamine* (**10b**)[7]. A mixture of 2.0 g of **10a** (5 mmol), 12 g of formic acid (98%; 50 mmol) and 14 g of formaldehyde (33%) was heated for 2 h at 100°. After cooling, the solid was filtered off and dissolved in CH_2Cl_2, and the resulting solution neutralized with $NaHCO_3$, washed with water and dried ($MgSO_4$). After evaporation of the solvent the crude residue (1.1 g, 51%) was recrystallized from CH_2Cl_2/petroleum ether: yellow-white crystals, m.p. 259°. – IR. ($CHCl_3$): 2880, 2845, 2805 (NCH_3); 1520, 1345 cm^{-1} (NO_2). – ^{1}H-NMR. ($CDCl_3$): 2.10 (*s*, 6 H); 7.8 (*m*, 12 H).

$C_{21}H_{18}N_4O_6$ (422.4) Calc. C 59.71 H 4.29 N 13.27% Found C 59.81 H 4.31 N 13.25%

p*K **Measurements.** – *Solvents.* Methylcellosolve was distilled twice from a mixture with CaO and BaO, eliminating each time a head fraction of 25%. The mixture with water (MCS) was made up by weight. Dioxane was refluxed with hydrochloric acid under N_2, then refluxed and distilled over Na. The mixture with water (Dx) was made up by weight. Acetonitrile (An) was refluxed and distilled successively, from NaH, P_2O_5 and CaH_2, with fractional distillation being the final purification. Nitrobenzene (Nb) was dried over P_2O_5 and distilled twice *in vacuo*. Acetic acid (Ac) was refluxed over CrO_3, then distilled and a head fraction of 25% was eliminated.

Apparatus. MCS: pH Meter *Metrohm* SE250 with a combined (glass-AgCl) microelectrode *Möller* (Zürich) NS-O-14. – Dx: *Metrohm* 'Titriscope' with a combined microelectrode *Metrohm* EA125X. – An, Nb, Ac: *Radiometer* 25 with scale expander PHA 925, using a glass electrode *Radiometer* G202C with a calomel reference electrode *Radiometer* K401, or a glass electrode *Metrohm* EA107X with a calomel electrode *Metrohm* EA204. The calomel electrode dipped in sat. aqueous KCl-solution, the junction with the titrating vessel being maintained by a saturated solution of KCl in acetic acid (for Ac) or methanol (for An, Nb). – The reaction vessel was thermostated at 25.0±0.1° and kept filled with N_2; magnetic stirring; piston buret of 10 ml *(Metrohm)*.

Potentiometric titrations. MCS, Dx: *ca.* 0.03 mmol of amine (*ca.* 10 mg) in 10 ml of solvent were titrated with 0.1N HCl in the mixed solvent. The scale was calibrated by titration of standard bases of known pK_a^{MCS} [12]. Before each measurement the electrode was conditioned in the solvent; after each measurement it was rinsed with water. Each MCS value given in the *Table* is the mean of 5 titrations; Dx: single measurements. – Ac: *ca.* 0.1 mmol of amine (*ca.* 30 mg) in 50 ml Ac were titrated with *ca.* 0.05N acid, prepared by adding 0.9 ml of 70% aqueous perchloric acid and 3 ml acetic anhydride to 100 ml of Ac; the acid was about 0.1N (controlled by titration). Scale calibration, by titration of *α*-naphthylamine of known pK_a^{Ac} [18], was repeated several times during the measurements. Each value in the *Table* is the mean of 3 titrations. – An: Quantities as with Ac; *ca.* 0.1N acid was prepared from 0.9 ml 70% aqueous $HClO_4$-solution and 100 ml An. Calibration (repeated from time to time) with 2 bases of known pK_a^{An} [47]; 3 titrations per base of the *Table*. – Nb: Quantities as with Ac; *ca.* 0.1N acid was prepared [17] by adding 0.9 ml of 70% aqueous perchloric acid to 3 ml of acetic anhydride, letting it react some minutes, adding 100 ml of Nb and letting it stand overnight. Calibration with 3 bases of known pK_a^{Nb} [11] was repeated several times during the measurements. Each value in the *Table* is the mean of 3 titrations.

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