How Delocalised are Resonance-stabilised 1-[4-(*N*-Methyl-*N*-alkylamino)phenyl]-2,2,2-trifluoroethyl Carbocations?

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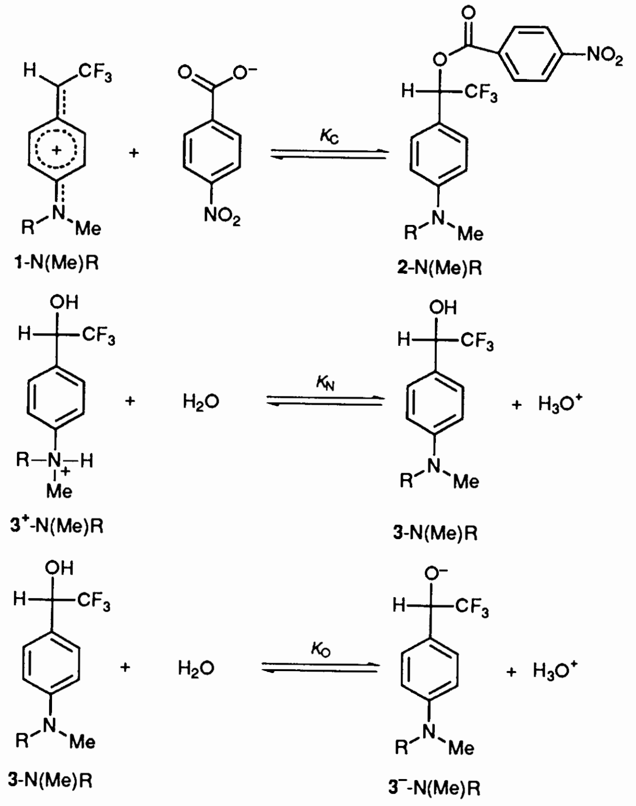
An *N*-trifluoroethyl for *N*-methyl substitution causes a $\geq 10^{4.1}$-fold increase in the equilibrium constant for the reaction of 4-$Me_2NArCH(CF_3)^+$ with 4-nitrobenzoate anion in 20% acetonitrile in water. The *N*-trifluoroethyl for *N*-methyl substitution causes a $10^{5.0}$-fold increase in the dissociation constant for loss of a proton from nitrogen at 4-$Me_2NH^+ArCH(CF_3)OH$, a reaction in which there is a *full unit decrease in charge at nitrogen*. These data show that the reaction of 4-$Me_2NArCH(CF_3)^+$ with 4-nitrobenzoate anion behaves as if there were a decrease in effective charge at nitrogen of ≥ 0.80 units on moving from the carbocation to the neutral nucleophile adduct 4-Me(R)$NArCH(CF_3)$(4-nitrobenzoate). The results suggest that the positive charge at these carbocations is largely localised at nitrogen, so that they more closely resemble iminium ions than benzyl carbocations.

The strongest interaction that can stabilise a carbocation is direct resonance electron donation which results in charge delocalisation onto the electron-rich substituent(s). The extent of such charge delocalisation at carbocations stabilised by electron-donating substituents has been estimated by calculation,[1,2] and by NMR experiments on persistent carbocations which compare the ^{13}C chemical shifts for the carbocation with the corresponding chemical shifts for a neutral derivative.[3,4]

We present here a new protocol for estimation of the extent of resonance electron delocalisation at reactive carbocations in nucleophilic solvents, and its application to 1-[4-(*N*-methyl-*N*-alkylamino)phenyl]-2,2,2-trifluoroethyl carbocations [**1**-N(Me)R, Scheme 1]. Resonance electron donation from nitrogen at **1**-N(Me)R is accompanied by the localisation of positive charge at nitrogen which will result in a destabilising interaction of this charge with a strongly electron-withdrawing trifluoroethyl 'reporter' substituent at nitrogen ($R = CH_2CF_3$). The strength of this interaction can be estimated from the effect of the $-CH_2CF_3$ group on the equilibrium constant K_C (Scheme 1) for a reaction in which this destabilising interaction is relieved in the products. The substituent effect will depend upon the separation between the positive end of the $-CH_2CF_3$ dipole and the centre of positive charge at **1**-N(Me)R. If the charge is localised at nitrogen, then the effect of the $-CH_2CF_3$ substituent on K_C will be close to the effect of a $-CH_2CF_3$ substituent on a reaction in which a localised positive charge is lost from the nitrogen (K_N, Scheme 1). However, if the charge is localised at the benzylic and the ring carbon atoms then the $-CH_2CF_3$ substituent effect on K_C will be closer to that for a reaction in which the change in charge occurs at a distant atom (*e.g.*, K_O, Scheme 1).

We report that the effect of an *N*-trifluoroethyl for *N*-methyl substitution on K_C for the reaction of **1**-NMe_2, is $\geq 80\%$ as large as the effect on K_N for the deprotonation of $\mathbf{3}^+$-N(Me)R. This result suggests that **1**-N(Me)R more closely resemble iminium ions than benzylic carbocations.



Scheme 1

Experimental

Materials.—Inorganic salts and organic chemicals used for syntheses were reagent grade and were used without further purification, unless noted otherwise. 2,2,2-Trifluoroethanol and 4-nitrobenzoic acid were purchased from Aldrich. Methanol and acetonitrile were HPLC grade purchased from Fisher. 4-Nitrobenzoic acid was recrystallised from ethanol. The water used for product and kinetic studies was distilled and then passed through a Milli-Q purification system.

Synthesis.—1-[4-(*N*,*N*-Dimethylamino)phenyl]-2,2,2-trifluoroethyl 4-nitrobenzoate (**2**-NMe_2),[5] 1-[4-(*N*,*N*-dimethylamino)phenyl]-2,2,2-trifluoroethyl 3,5-dinitrobenzoate[5] and 1-{4-[*N*-methyl-*N*-(2,2,2-trifluoroethyl)amino]phenyl}-2,2,2-trifluoroethyl pentafluorobenzoate[6] were prepared as described previously.

1-{4-[N-*Methyl*-N-(2,2,2-*trifluoroethyl*)*amino*]*phenyl*}-2,2,2-*trifluoroethyl* 4-*nitrobenzoate* [**2**-N(Me)CH_2CF_3]. This was prepared by esterification of 1-{4-[*N*-methyl-*N*-(2,2,2-trifluoro-

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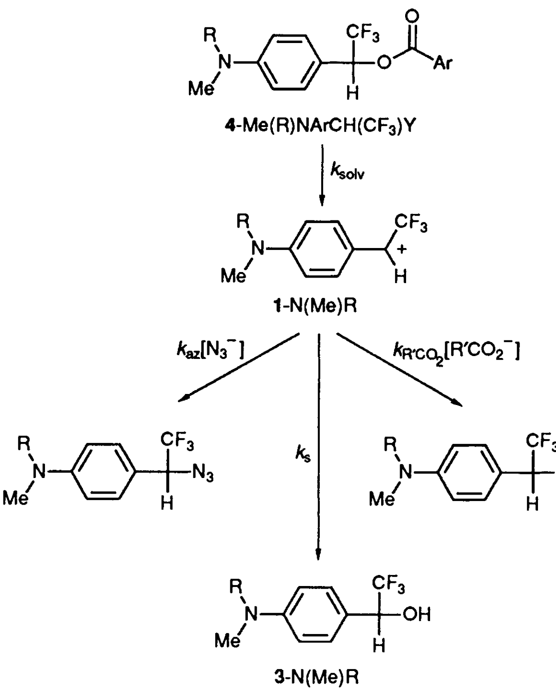


Scheme 2

ethyl)amino]phenyl}-2,2,2-trifluoroethanol [3-N(Me)CH$_2$CF$_3$] with 4-nitrobenzoic acid by adaptation of a published procedure.[6] This gave the *ester* in 74% yield as a yellow gum. *J* values are given in Hz (Found: C, 49.7; H, 3.3; N, 6.4. $C_{18}H_{14}F_6N_2O_4$ requires C, 49.55; H, 3.2; N, 6.4%); δ_H(200 MHz, CDCl$_3$) 8.30 (4 H, m, ArNO$_2$), 7.45 (2 H, d, *J* 9, Ar), 6.83 (2 H, d, *J* 9, Ar), 6.30 (1 H, q, *J* 7, CH), 3.89 (2 H, q, *J* 9, CH$_2$), 3.08 (3 H, s, CH$_3$).

Preparation of Solutions.—Solutions containing sodium acetate were prepared by mixing an aqueous solution of sodium acetate with acetonitrile and aqueous NaClO$_4$ to give a final solvent of 20% acetonitrile in water (I = 0.80, NaClO$_4$). Solutions containing sodium 4-nitrobenzoate were prepared by neutralisation of an aqueous solution of 4-nitrobenzoic acid with sodium hydroxide, and then mixing this solution with acetonitrile and aqueous NaClO$_4$ to give a final solvent of 20% acetonitrile in water (I = 0.80, NaClO$_4$).

Kinetic Studies.—Rate constants were determined at 25 °C in 20% acetonitrile in water (I = 0.80, NaClO$_4$) in the presence of *ca.* 0.01 mol dm^{-3} sodium azide. Reactions were initiated by making a 100-fold dilution of a solution of substrate in acetonitrile into the reaction mixtures. The rate constant for solvolysis of **2**-NMe$_2$ (3×10^{-5} mol dm^{-3}) was determined spectrophotometrically by monitoring the decrease in absorbance at 264 nm. The rate constant for solvolysis of **2**-N(Me)CH$_2$CF$_3$ (2×10^{-5} mol dm^{-3}) was determined by monitoring the disappearance of reactant by HPLC, with 3-(4-methoxyphenyl)propan-1-ol (5×10^{-4} mol dm^{-3}) as an injection standard and peak detection at 250 nm. Pseudo-first-order rate constants, k_{obsd}, were obtained from the slopes of linear semilogarithmic plots of reaction progress against time, which covered at least 3 reaction half-times. Rate constants were reproducible to ±5%.

Product Studies.—Product studies were performed at room temperature (22 ± 2 °C) in 20% acetonitrile in water (I = 0.80, NaClO$_4$). Reactions were initiated by making a 100-fold dilution of a solution of substrate in acetonitrile into the reaction mixtures to give a final substrate concentration of (1–2) × 10^{-5} mol dm^{-3}. In cases where one or more of the products were unstable over extended reaction times it was shown that the ratios of product yields determined at early reaction times were constant.

The products of nucleophilic substitution were separated by HPLC as described previously[5,7] and were detected by the UV absorbance of the respective aromatic rings at the following wavelengths: 4-Me$_2$NArCH(CF$_3$)Y, 254 nm; 4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)Y, 253 nm. The ratios of product yields obtained by HPLC analysis were reproducible to ±10%.

Nucleophile Selectivities.—Nucleophile selectivities, k_{Nu1}/k_{Nu2}, for the reactions of XArCH(CF$_3$)Y with Nu1 and Nu2 were calculated from the ratios of the peak areas of the two nucleophile adducts determined by HPLC analyses, according to eqn. (1), where $\varepsilon_2/\varepsilon_1$ is the ratio of the extinction coefficients for the two adducts at the wavelength used for the HPLC analysis.

$$k_{Nu1}/k_{Nu2} = \frac{\varepsilon_2[\text{area}]_{RNu1}[Nu_2]}{\varepsilon_1[\text{area}]_{RNu2}[Nu_1]} \qquad (1)$$

The ratios of extinction coefficients for the nucleophile adducts were determined as described in previous work.[5,7] Ratios of $\varepsilon_1/\varepsilon_2 = 1.0$ were determined for 4-Me$_2$NArCH(CF$_3$)Y and 4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)Y when Y = OH, N$_3$ and O$_2$CCH$_3$.[5,6] Ratios of $\varepsilon_1/\varepsilon_2$ = 1.6 and 1.15 were determined respectively for the extinction coefficients of 4-Me$_2$NArCH(CF$_3$)(4-nitrobenzoate) and 4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)(4-nitrobenzoate) relative to the corresponding adducts with acetate ion.

*p*K*$_a$ Determinations.*—The pK_as in water for the loss of a proton from oxygen at **3**-N(Me)R were determined spectrophotometrically, following a published procedure,[8] by monitoring the decrease in absorbance at 255 nm and 254 nm due to formation of **3**$^-$-NMe$_2$ and **3**$^-$-N(Me)CH$_2$CF$_3$, respectively. The pK_as in water for loss of a proton from nitrogen at **3**$^+$-N(Me)R were determined spectrophotometrically by monitoring the increase in absorbance at 255 nm and 254 nm due to formation of **3**-NMe$_2$ and **3**-N(Me)CH$_2$CF$_3$. **3**$^+$-N(Me)CH$_2$CF$_3$ was generated in solutions of HCl whose effective acidities were determined using the H_0''' scale.[9]

Results

Rate constant ratios for partitioning of the carbocation intermediates[5,6] of the reactions of 4-Me$_2$NArCH(CF$_3$)(3,5-dinitrobenzoate) and 4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)(pentafluorobenzoate) between capture by different nucleophiles in 20% acetonitrile in water (Scheme 2), determined from the ratios of the yields of the nucleophile adducts, are reported in Table 1.

The first-order rate constants k_{solv} for the solvolysis reactions of **2**-N(Me)R in 20% acetonitrile in water at 25 °C are reported in Table 2. These reactions were carried out in the presence of low concentrations ($\leq$0.01 mol dm^{-3}) of the strong nucleophile azide ion, in order to eliminate the inhibition of the reaction due to the capture of the carbocation intermediate by the product leaving group ion; azide ion is a much more reactive nucleophile than 4-nitrobenzoate ion (Table 1). The values of k_{obsd} for the reactions of **2**-NMe$_2$ or **2**-N(Me)CH$_2$CF$_3$ remain constant for an increase from 0.001 to 0.01 mol dm^{-3} azide ion. Under these reaction conditions, the azide adducts are the only detectable products.

Values of the equilibrium constants for the loss of the hydroxyl proton from **3**-N(Me)R (K_O) and the loss of the anilinium proton from **3**$^+$-N(Me)R (K_N) in water were deter-

Table 1 Product rate constant ratios for the reactions of 4-Me(R)NArCH(CF$_3$)Y with carboxylate and azide ions and solvent in 20% acetonitrile in water (Scheme 2)[a]

Ratio	4-Me$_2$NArCH(CF$_3$)-(3,5-dinitrobenzoate)	4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)-(pentafluorobenzoate)
k_{AcO}/k_s (dm^3 mol^{-1})	79[b]	24[c]
$k_{4\text{-NB}}/k_{AcO}$[d]	0.79[e]	1.2[f]
k_{az}/k_{AcO}	4.8×10^4[g]	6.2×10^3[h]
k_{az}/k_s (dm^3 mol^{-1})	3.8×10^6[i]	1.5×10^5[i]

[a] At 22 ± 2 °C and $I = 0.80$ (NaClO$_4$) and determined by product analysis by HPLC. [b] Average of values determined in acetate buffers at [AcO$^-$] = 0.051 mol dm^{-3} (95% free base) and 0.057 mol dm^{-3} (85% free base). [c] Average of values determined in acetate buffers at [AcO$^-$] = 0.063 mol dm^{-3} (95% free base) and 0.057 mol dm^{-3} (85% free base). [d] $k_{4\text{-NB}}$ is the rate constant for reaction of 4-nitrobenzoate anion. [e] Average of eight determinations in acetate buffers at [AcO$^-$] = 0.051 mol dm^{-3} (95% free base) or 0.057 mol dm^{-3} (85% free base) and four values of [4-NO$_2$ArCO$_2^-$] in the range 0.05–0.15 mol dm^{-3}. [f] Average of eight determinations in acetate buffers at [AcO$^-$] = 0.063 mol dm^{-3} (95% free base) or 0.057 mol dm^{-3} (85% free base) and four values of [4-NO$_2$ArCO$_2^-$] in the range 0.033–0.13 mol dm^{-3}. [g] Average of 10 determinations in acetate buffers at [AcO$^-$] = 0.48 or 0.71 mol dm^{-3} (95% free base) and five values of [N$_3^-$] in the range 5×10^{-5}–1.5×10^{-4} mol dm^{-3}. [h] Average of 10 determinations in acetate buffers at [AcO$^-$] = 0.48 or 0.71 mol dm^{-3} (95% free base) and five values of [N$_3^-$] in the range 1×10^{-4}–2×10^{-3} mol dm^{-3}. [i] $(k_{AcO}/k_s)(k_{az}/k_{AcO})$.

Table 2 Rate and equilibrium constants for reactions of 4-Me(R)NArCH(CF$_3$)$^+$ with 4-nitrobenzoate anion in 20% acetonitrile in water[a]

$$\text{4-NO}_2\text{ArCO}_2^- + \text{4-Me(R)NArCH(CF}_3)^+ \xrightleftharpoons[k_{solv}]{k_{4\text{-NB}}} \text{4-Me(R)NArCH(CF}_3)\text{O}_2\text{CArNO}_2$$

Product	k_{solv}[b]/ s^{-1}	$k_{4\text{-NB}}$[c]/ dm^3 mol^{-1} s^{-1}	K_C[d]/ dm^3 mol^{-1}
4-Me$_2$NArCH(CF$_3$)(4-nitrobenzoate)	9.5×10^{-4}	$\leq 1.6 \times 10^4$[e]	$\leq 1.7 \times 10^7$
4-Me(CF$_3$CH$_2$)NArCH(CF$_3$)(4-nitrobenzoate)	4.3×10^{-6}	1.0×10^6[f]	2.3×10^{11}

[a] At 25 °C and $I = 0.80$ (NaClO$_4$). [b] The observed first-order rate constant for solvolysis of the 4-nitrobenzoate adduct. [c] The second-order rate constant for capture of the carbocation by 4-nitrobenzoate anion. [d] $k_{4\text{-NB}}/k_{solv}$. [e] Calculated from the data in Table 1 and $k_{az} \leq 1 \times 10^9$ dm^3 mol^{-1} s^{-1} (see text). [f] Calculated from the data in Table 1 and $k_{az} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1} (see text).

Table 3 Equilibrium constants for the reactions of 4-Me(R)NArCH(CF$_3$)$^+$, 4-Me(R)NH$^+$ArCH(CF$_3$)OH and 4-Me(R)NArCH(CF$_3$)OH (Scheme 1)[a]

Reaction	K_C, K_N or K_O		
	R = Me	R = CH$_2$CF$_3$	$\Delta \log K$
Y$^-$ + 4-Me(R)NArCH(CF$_3$)$^+$ $\rightleftharpoons$ 4-Me(R)NArCH(CF$_3$)Y[b]	$\leq 1.7 \times 10^7$ dm^3 mol^{-1}	2.3×10^{11} dm^3 mol^{-1}	≥ 4.1
4-Me(R)H$\overset{+}{\text{N}}$ArCH(CF$_3$)OH $\rightleftharpoons$ 4-Me(R)NArCH(CF$_3$)OH + H$^+$[c]	6.3×10^{-5} mol dm^{-3}	0.5 mol dm^{-3}	5.0
4-Me(R)NArCH(CF$_3$)OH $\rightleftharpoons$ 4-Me(R)NArCH(CF$_3$)O$^-$ + H$^+$[c]	4.3×10^{-13} mol dm^{-3}	7.4×10^{-13} mol dm^{-3}	0.24

[a] At 25 °C. [b] In 20% acetonitrile in water ($I = 0.80$, NaClO$_4$) with Y$^-$ = 4-nitrobenzoate anion (Table 2). [c] Determined in water by spectrophotometric titration.

mined by spectrophotometric titration and are reported in Table 3. The difference in the acidities of **3**$^+$-NMe$_2$ and **3**$^+$-N(Me)CH$_2$CF$_3$ (5.0 pK_a units) is similar to the difference in the acidities of ethylamine and 2,2,2-trifluoroethylamine (5.1 pK_a units).[10] The difference in the acidities of **3**$^+$-NMe$_2$ and **3**$^+$-N(Me)CH$_2$CF$_3$ in 20% acetonitrile in water will be very close to the difference observed in water, because this represents only a small change in solvent, and the effects of changing solvent on substituent effects on amine pK_a are, in turn, small. For example, there is only a small decrease in the Hammett ρ value from $\rho = 3.43$ to $\rho = 3.26$ for deprotonation of ring substituted anilinium ions when the solvent is changed from 82% dioxane in water to 20% dioxane in water.[11]

Discussion

We have shown in earlier work that 4-Me(R)NArCH(CF$_3$)Y (R = CH$_3$, CH$_2$CF$_3$) react by a D$_N$ + A$_N$ (S$_N$1) mechanism through the liberated carbocation intermediates **1**-N(Me)R (Scheme 2).[5] The rate constant for the capture of **1**-N(Me)-CH$_2$CF$_3$ by azide ion is very close to the diffusion limit ($k_{az} \sim 5 \times 10^9$ dm^3 mol^{-1} s^{-1}), while the value of k_{az} for the capture of **1**-N(Me)$_2$ must be at least four-fold smaller than this diffusional value.[6] An α-CF$_3$ for α-CH$_3$ substitution at XArCH(CH$_3$)$^+$ (X = 4-OMe, 4-SMe) has only a small effect on the rate constants k_s and k_{AcO} for carbocation capture by solvent and acetate ion, respectively.[5,12] Therefore k_{az} for the reaction of **1**-NMe$_2$ may be as small as the value of $k_{az} = 2 \times 10^7$ dm^3 mol^{-1} s^{-1} determined by direct measurement for the reaction of 4-Me$_2$NArCH(CH$_3$)$^+$.[13]

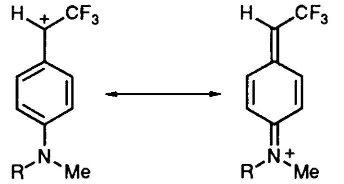
Absolute rate constants $k_{4\text{-NB}}$ for the capture of **1**-N(Me)R by 4-nitrobenzoate anion reported in Table 2 were calculated from the rate constant ratios in Table 1 for partitioning of the carbocation intermediates [**1**-N(Me)R] of the solvolysis reactions of 4-Me(R)NArCH(CF$_3$)Y and values of $k_{az} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1} for the reaction of **1**-N(Me)CH$_2$CF$_3$ or $k_{az} \leq 1 \times 10^9$ dm^3 mol^{-1} s^{-1} for the reaction of **1**-NMe$_2$ (Table 2). The equilibrium constants K_C (Scheme 1) for the reaction of **1**-N(Me)R with 4-nitrobenzoate anion were calculated as the ratio of rate constants for reaction in the forward and reverse directions, $k_{4\text{-NB}}/k_{solv}$, where k_{solv} is the first-order rate constant for the solvolysis of **2**-N(Me)R by a stepwise mechanism, in which ionisation of the substrate is the rate-determining step. The upper limit of $k_{az} = 1 \times 10^9$ dm^3 mol^{-1} s^{-1} for the reaction of **1**-NMe$_2$ with azide ion has been used in Tables 2 and 3, in order to report the most conservative estimate of the effect of the *N*-trifluoroethyl substituent on K_C (Scheme 1). Use of the smaller value of $k_{az} = 2 \times 10^7$ dm^3 mol^{-1} s^{-1} for this carbocation would have given a 50-fold larger substituent effect.

The value of $\Delta \log K_C = \geq 4.1$ from Table 3 is nearly as large as the value of $\Delta \log K_N = 5.0$ for the loss of a proton from **3**$^+$-N(Me)R, but it is much larger than the value of $\Delta \log K_B = 0.5$ for a hypothetical reaction in which there is a full unit decrease in charge at the benzylic carbon of **3**-N(Me)R. The value of $\Delta \log K_B$ was calculated from $\Delta \log K_O = 0.24$ (Table 3) and an attenuation factor of 2 for movement of the charge one atom closer to the reaction centre.[14]

The data in Table 3 show that the inductive effect of the –CH$_2$CF$_3$ substituent on $\log K_C$ is $\geq 80\%$ as large as the substituent effect on $\log K_N$ for a reaction in which a full positive charge* is lost at the nitrogen. That is, the reactions of **1**-N(Me)R with nucleophilic reagents behave as if an effective charge of ≥ 0.8 is lost from the nitrogen, using deprotonation of **3**$^+$-N(Me)R as the reference reaction.

This treatment will also underestimate the change in effective charge at **1**-N(Me)R upon reaction with the 4-nitrobenzoate anion, if the *N*-trifluoroethyl substituent effect on K_c is attenuated by a shift in charge at **1**-N(Me)CH$_2$CF$_3$ away from the ring nitrogen and towards the benzylic carbon. In any case, the large apparent effective charge at nitrogen of **1**-N(Me)R suggests that the structure of this species more closely resembles that of an iminium ion than that of a benzylic carbocation.

1-N(Me)R react with nucleophilic reagents as benzylic carbocations (addition to C-α) rather than as iminium ions (addition to the C-4 ring position.[6,15] This shows that the intrinsic reactivity of a cationic benzylic centre is so much greater than that of an iminium ion, that exclusive nucleophilic addition to the benzylic carbon is observed even when the iminium ion is the dominant resonance structure.



The data in Table 3 show qualitatively that the centre of positive charge at **1**-N(Me)R lies relatively close to the nitrogen. The exact centre of charge might be determined from the weighted averages of the fractional charges at nitrogen, the benzylic carbon, and the two ring carbons *ortho* to the benzylic carbon, but there are insufficient data to evaluate these fractional charges.

It has been estimated by *ab initio* calculations for the (4-dimethylamino)benzyl carbocation that the transfer of 0.28 π-electrons from the 4-amino substituent to the benzylic carbon places a charge of only +0.28 at the nitrogen.[2] The large inductive effect of the –CH$_2$CF$_3$ substituent on K_C (Table 3) suggests that there is a substantially larger positive charge at the nitrogen of **1**-N(Me)R. This provides further evidence for an unusually large resonance stabilisation of α-CF$_3$ substituted benzyl carbocations.[5,15–17] A major driving force for charge delocalisation at 4-XArCH(CF$_3$)$^+$ is the relief of destabilising charge–dipole interactions which accompanies movement of the centre of positive charge away from the dipole of the α-CF$_3$ group.[5,18]

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* Or slightly less than a full charge, if water hydrogen bonded to the anilinium proton bears a small positive charge.