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Super acidifiers: the origin of the exceptional electron transmission capability of the SO_2CF_3 group in carbanion stabilization†

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Received 25th February 2003, Accepted 1st April 2003
First published as an Advance Article on the web 16th April 2003

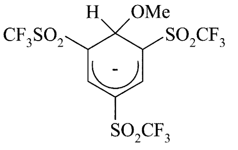
As part of studies aimed at clarifying conflicting reports concerning the acidifying effects exerted by the SO_2CF_3 *vs.* NO_2 moieties with respect to carbanion stabilities, we have investigated the ionization equilibria of an extended set of benzyltriflones and have determined both pK_a values of the carbon acids and ^1H and ^{13}C NMR parameters of the resulting carbanions. Acidities determined in H_2O–Me_2SO mixtures and in pure Me_2SO show a contrasting behaviour between 4-X-substituted benzyl triflones and related arylnitromethanes. While the latter exhibit a decreasing acidity on going from H_2O to Me_2SO media, the benzyltriflone analogues show in fact increasing acidity in Me_2SO. This opposing trend suggests that the exocyclic α-SO_2CF_3 moiety is strongly stabilizing the negative charge of the carbanions through polarizability effects favored by the dipolar aprotic Me_2SO solvent. As a result, inversions in the acidity sequences of α-NO_2 and α-SO_2CF_3 activated carbon acids are observed on going from H_2O to Me_2SO. ^1H and ^{13}C NMR data are in full accord with the conclusion that only little negative charge is transferred to the 4-X-substituted phenyl ring upon ionization. Increasing further the ring substitution by electronegative groups to 2,4- and 2,4,6- patterns, enhances the charge transfer but this nevertheless remains moderate even with the most activated 2,4,6- trinitro or 2,6-dinitro-4-SO_2CF_3 sequences. Altogether, our results provide convincing evidence of the unusual electron transmission ability of the very strongly acidifying SO_2CF_3 group.

Traditionally the nitro group has been considered as the electron-withdrawing moiety *par excellence* throughout the domain of organic chemistry. In synthesis, as well as in reactivity studies, countless examples have been recorded where the NO_2 group plays a pivotal role.[1] Indeed, even within the past ten years, a number of books as well as numerous reviews have described various aspects of nitro-organic chemistry.[2] However, the recognition that other moieties could have an even greater electron-withdrawing power than the NO_2 group has raised interest for several decades.[3,4]

In particular, a major leap from the NO_2 group in acidifying power came about with introduction of the SO_2CF_3 group in the '60s and the finding by Sheppard and Yagupolskii that this substituent is significantly more efficient than a NO_2 group in promoting ionization of benzoic acids, the reference AH-type acids for the attribution of Hammett substituent constants in aqueous solution.[4,5] Studies of these acid–base reactions have yielded the following Hammett substituents constants for SO_2CF_3: $\sigma_m = 0.76$, $\sigma_p = 0.96$.[6] These values compare with the following for NO_2: $\sigma_m = 0.71$, $\sigma_p = 0.81$.[6] Based on the results obtained for the ionization of anilinium ions and phenols, a σ_p^- value was equally attributed to the SO_2CF_3group, $\sigma_p^- = 1.65$, which compares with $\sigma_p^- = 1.24$ for NO_2 (reference anilinium ions).[6]

It is noteworthy that most of the efforts presently devoted to the design of new electron-acceptor super substituents are based on modifying the SO_2CF_3 group and replacing the oxygen atoms by intrinsically more electron-withdrawing moieties.[7–9] It becomes essential, therefore, to have a solid foundation of the modes of action which are responsible for the particular properties of the SO_2CF_3 group. It is the purpose of the present paper to shed some experimental evidence on this subject which has so far been addressed essentially through theoretical studies.[10–14]

In fact, the literature contains a number of conflicting reports regarding assessment of the electron-withdrawing effect of the SO_2CF_3 group. Importantly, but perhaps not surprisingly, some of these conflicting reports arise from the nature of the medium where the reactions were conducted as well as from structural effects with respect to the bonding site of the SO_2CF_3 group. In agreement with the substituent constants derived from the aforementioned studies, the SO_2CF_3 group is found to be markedly more activating than a NO_2 group in nucleophilic aromatic substitutions and in σ-complex formation processes.[15–18]



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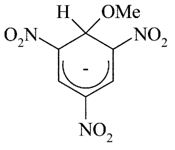

2

CH_3-X

3 : X = SO_2CF_3
4 : X = NO_2

As an example, the methoxide adduct **1** of tris(1,3,5-trifluoromethanesulfonyl)benzene is 10^6 times more stable thermodynamically than the trinitro analogue **2** in methanol.[16b] However, contrasting with these results, Bordwell has reported that trifluoromethanesulfonylmethane **3** and benzyltriflone **5a** (eqn. 1) are two carbon acids which are less acidic than the corresponding nitro derivatives, *i.e.* nitromethane **4** and phenylnitromethane **6a**, by two p*K* units in Me_2SO solution.[19] It is noteworthy that the bonding situation of the ionization site with respect to the SO_2CF_3 or NO_2 group in these systems differs from that in the other acid–base processes quoted above. On the other hand, measurements in the gas phase surprisingly indicate that trifluoromethanesulfonylmethane is about 7 p*K* units more acidic than nitromethane, contrary to the generally observed results that acidities in DMSO and in the gas phase follow a similar order.[7]

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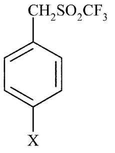
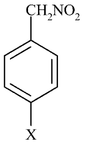
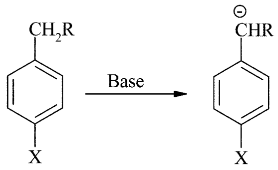
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR data of benzyltriflones **5a–e** and **9a–f** and their related carbanions in Me_2O solution. See http://www.rsc.org/suppdata/ob/b3/b302029k/

DOI: 10.1039/b302029k

Table 1 Changes in representative chemical shifts ($\Delta\delta H\alpha$, $\Delta\delta C\alpha$, $\Delta\delta C_4$, $\Delta\delta F\alpha$) and Coupling Constants ($\Delta^1J_{C\alpha H\alpha}$) upon ionization of 4-X-substituted benzyltriflones **5a–e** and related carbon acids in Me_2SO solution[a]

Structure	X	Compound	$\delta H\alpha$	$\Delta\delta H\alpha$	$\delta C\alpha$	$\Delta\delta C\alpha$	$^1J_{C\alpha H\alpha}$	$\Delta^1J_{C\alpha H\alpha}$	δC_4	$\Delta\delta C_4$	δF (SO_2CF_3)	$\Delta\delta F$
	H[b]	**5a**	5.25	—	54.80	—	142.77	—	129.61	—	−79.06	—
		C-**5a**	3.38	−1.87	55.02	0.22	163.89	21.12	116.85	−12.76	−80.81	−1.75
	CF_3	**5b**	5.44	—	54.02	—	142.42	—	130.02	—	−72.05	—
		C-**5b**	3.61	−1.83	57.65	3.63	166.15	23.73	115.89	−14.13	−74.58	−2.53
	CN	**5c**	5.46	—	54.31	—	143.41	—	112.43	—	−78.75	—
		C-**5c**	3.69	−1.77	60.20	5.89	167.42	24.01	95.58	−16.85	−81.58	−2.93
	NO_2[b]	**5d**	5.53	—	53.74	—	143.15	—	148.14	—	−79.18	—
		C-**5d**	4.07	−1.46	65.72	11.98	168.02	24.87	131.45	−16.69	−81.32	−2.14
	SO_2CF_3	**5e**	5.56	—	53.82	—	143.00	—	130.48	—	−71.97	—
		C-**5e**	4.06	−1.50	65.15	11.33	169.00	26.00	110.06	−20.42	−75.01	−3.04
	H[c]	**6a**	5.71	—	79.3	—	146.00	—	132.48	—	—	—
		C-**6a**	6.70	0.99	109.2	29.9	175.2	29.2	123.00	−9.48	—	—
	NO_2[d]	**6d**	5.95	—	77.55	—	149.1	—	148.02	—	—	—
		C-**6d**	6.84	0.89	109.76	32.21	180.11	31.3	140.09	−7.93	—	—

[a] δ in ppm relative to internal $SiMe_4$; J in Hz; Solvent [$^2H_2$] Me_2SO; [b] Ref. 20; [c] Ref. 26; [d] Ref. 25.

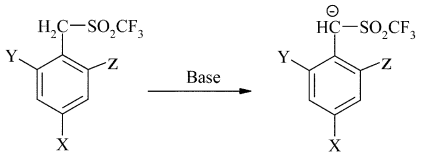


(1)

5 R= SO_2CF_3 C-5
6 R= NO_2 C-6
7 R= CN C-7
8 R= H C-8

(a) X=H; (b) X= CF_3; (c) X=CN; (d) X= NO_2; (e) X= SO_2CF_3

As part of continuing studies concerned with solvent effects on carbon acidities,[20] we have undertaken a study of the ionization equilibria of a number of monosubstituted benzyltriflones **5a–e** (eqn. 1), and polysubstituted ones **9a–f** (eqn. 2). These have been designed so as to bring into play opposing influences of exocyclic *versus* ring substitution of SO_2CF_3. As will be seen, combining the information obtained from a thermodynamic and NMR analysis of the equilibria shown in eqns 1 and 2 has revealed the importance of the solvent in determining the relative acidifying effects of SO_2CF_3 and NO_2 groups. Our results also shed light on fundamental aspects of electronic transmission in the molecules under investigation.



(2)

9 C-9

a) X = CF_3, Y = NO_2, Z = H
b) X = Y = NO_2, Z = H
c) X = SO_2CF_3, Y = NO_2, Z = H
d) X = CF_3, Y = Z = NO_2
e) X = Y= Z = NO_2
f) X = SO_2CF_3, Y = Z = NO_2

Results

Structural studies

Addition of dilute Me_4NOH solutions to ~3–5 × 10^{-5} mol dm^{-3} solutions of the triflones **5a–e** and **9a–f** in pure Me_2SO resulted in the reversible and complete formation of species exhibiting intense absorption maxima at the wavelengths quoted in Tables 3 and 4. Provided that the ionization process could be effectively achieved at the solvent composition at hand, similar reversible changes were observed in H_2O–Me_2SO mixtures containing 30, 50, 70 and 90% Me_2SO by volume. Unambiguous evidence that base addition to **5a–e** and **9a–f** actually afforded the expected carbanions **C-5a–e** and **C-9a–f** was obtained by carrying out ^1H, ^{13}C and ^{19}F NMR studies of the ionization reactions in Me_2SO. Data which are relevant to our discussion are collected in Tables 1 and 2 while other chemical shift data is given as Electronic supplementary information (Tables S1–S3).† To be noted is that the results pertaining to the ionization of **5a**, **5c**, **9b** and **9e** were available from a previous study of these derivatives.[20]

Equilibrium measurements

Using appropriate and previously standardized buffers (carboxylic acids, phenols and amines),[21,22] the pK_a values of **5a–e** and **9a–f** in the various H_2O–Me_2SO mixtures studied were determined from the observed absorbance changes at λ_{max} of the conjugate carbanions obtained at equilibrium as a function of pH. As illustrated in Fig. 1, these changes described regular acid–base type equilibrations, excellent straight lines with unit slopes being obtained on plotting the log values of the ratio of the concentrations of ionized (C^-) to non ionized (CH) triflones as a function of pH (eqn. 3). The pK_a values thus obtained at 25 °C and constant ionic strength of 0.5 mol dm^{-3} (NMe_4Cl) are summarized in Tables 3 and 4.

$$pH = pKa + \log\frac{[C^-]}{[CH]} \qquad (3)$$

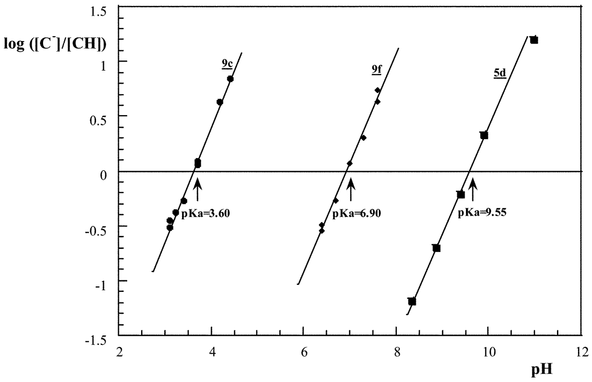
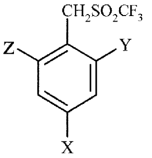


Fig. 1 Effect of pH on the ionization of the benzyltriflones **9f** in water, **5d** in 30–70 (v/v) H_2O–Me_2SO and **9c** in 10–90 (v/v) H_2O–Me_2SO at 25 °C. Each of the three lines is based on the acidity scale pertaining to the corresponding solvent.

Table 2 Changes in representative chemical shifts (ΔδHα, ΔδHα, ΔδCα) and coupling constants ($\Delta^1J_{C\alpha H\alpha}$) upon ionization of 2,4,6-Y,X,Z-substituted benzyltriflones **9a–f** in Me_2SO solution[a]

Structure	X	Y	Z	Compound	δHα	ΔδHα	δCα	ΔδCα	$^1J_{C\alpha H\alpha}$	$\Delta^1J_{C\alpha H\alpha}$	δC_4	$\Delta\delta C_4$	δF	ΔδF
	CF_3	NO_2	H	**9a**	5.80	—	51.97	—	145.24	—	131.52	—	−73.16	—
				C-**9a**	5.52	−0.28	66.22	14.25	176.56	31.32	114.64	−16.88	−75.40	−2.24
	NO_2	NO_2	H	**9b**[b]	5.87	—	51.99	—	145.33	—	148.42	—	78.18	—
				C-**9b**[b]	5.78	−0.09	72.25	20.26	176.98	31.65	134.12	−19.30	−79.35	−1.17
	SO_2CF_3	NO_2	H	**9c**	5.91	—	52.03	—	145.54	—	132.16	—	−73.08	—
				C-**9c**	5.74	−0.17	73.15	21.12	176.32	32.78	110.27	−21.89	−74.69	−1.61
	CF_3	NO_2	NO_2	**9d**	5.79	—	47.70	—	145.20	—	132.00	—	−76.81	—
				C-**9d**	4.98	−0.81	59.39	11.69	170.80	25.60	113.10	−18.90	−79.00	−2.19
	NO_2	NO_2	NO_2	**9e**[b]	5.83	—	48.96	—	146.60	—	149.27	—	−76.76	—
				C-**9e**[b]	5.82	−0.01	73.46	24.50	172.20	25.60	130.70	−18.57	−78.93	−2.17
	SO_2CF_3	NO_2	NO_2	**9f**	5.84	—	48.13	—	145.80	—	133.32	—	−72.13	—
				C-**9f**	5.87	−0.03	76.85	28.72	173.50	27.70	106.22	−27.10	−74.24	−2.11

[a] δ in ppm relative to internal $SiMe_4$, J in Hz; Solvent [$^1H_2$] Me_2SO; [b] Ref. 20.

The $pK_a^{Me_2SO}$ values of **5a** and **5c** were known from previous works by Bordwell *et al.*[19] The ionization of all other triflones, in pure Me_2SO solution, *i.e.* **5b**, **5d**, **5e** and **9a–f** was found to occur in pH ranges covered by various amines buffers.[23] Accordingly, $pK_a^{Me_2SO}$ the values were determined according to the same methodology as that used in H_2O–Me_2SO mixtures. The results are also given in Tables 3 and 4.

Discussion

Electronic transmission of SO_2CF_3 *vs.* NO_2 as exhibited in ionization of α-nitro and α- SO_2CF_3 benzylic carbon acids

Equilibrium acidities. Fig. 2 illustrates the contrasting solvent dependence of H_2O–DMSO composition on the acidities of unsubstituted and 4-X-substituted benzyltriflones **5a–e** as compared with that of related phenylnitromethanes (**6a**, **6d**) and nitromethane **4**. As can be seen, a major difference in the two series is their different response to the solvent changes. *While for the triflones the acidity increases with increasing Me_2SO content the opposite trend prevails with phenylnitromethanes.*

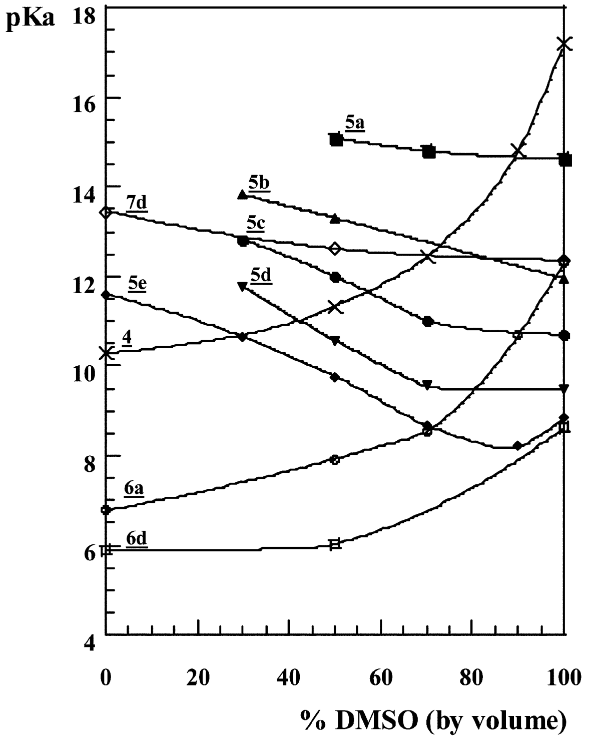


Fig. 2 Effect of a H_2O–Me_2SO transfer on the acidity of 4-X-substituted benzyltriflones and some related α-nitro- and α-cyano-activated carbon acids.

In the case of the phenylnitromethane series, it has been recognized that the resonance structure **6-B** with the charge essentially delocalised on the nitronate oxygens is by far the main contributor to the stabilization of the conjugate carbanions, **C-6**, including when X = NO_2. [24–28] It follows that on changing from H_2O to Me_2SO, this will be accompanied by loss of H-bonding solvation of this nitronate moiety, and hence by a decrease in the stability of the carbanion structure.[27] This accounts for the observed decrease in acidity of the α-nitro-activated carbon acids in general and of compounds **4**, **6a** and **6d** in the context of Fig. 2 in particular.

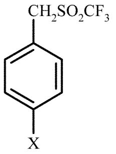
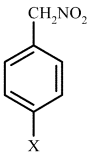
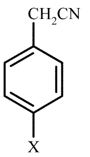
On the other hand, the reverse trend in solvent effects on acidity that is observed with triflones **5a–e** is in accord with the idea that in this case structure **5A** contributes predominantly to the stabilization of the carbanions **C-5a–e**, the negative charge on carbon being stabilized through charge polarization effects.[29–32]

As is now recognized following various theoretical studies, structure **5B**, implying the capability of the SO_2CF_3 group to delocalize charge by resonance (–M) does not play a significant role.[10–13,29,30] On the other hand, as will be elaborated on below, resonance structures of type **5C**, **5D** and, of course **5E**, can be only of minor importance in determining the stability of the related carbanions.

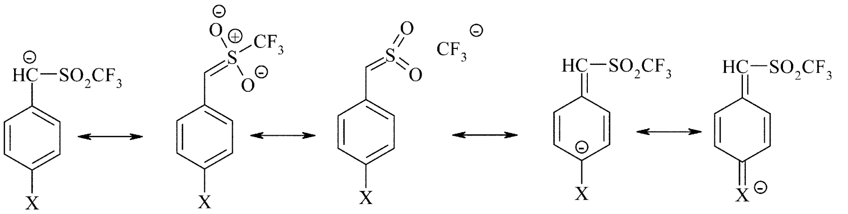
As a consequence of the differing responses of the activating effects of the α-SO_2CF_3 and α-NO_2 groups of the various carbon acids studied to the solvent changes, significant variations in the relative acidities of some of these compounds arise on going from water to Me_2SO. Thus, the unsubstituted benzyltriflone **5a** is 7 pK units less acidic than phenylnitromethane **6a** in 50% H_2O–50% Me_2SO but the acidity difference between these two substrates falls to 2 pK units in pure Me_2SO. Interestingly, the solvent effects lead to noteworthy inversions in the acidity of some compounds, as can be seen for example in comparing the plots referring to phenylnitromethane **6a** and the 4-nitro-substituted benzyltriflone **5d** in Fig. 2. From a much stronger acidity of **6a** in 30% Me_2SO ($\Delta pKa \sim 4.2$), one comes to similar acidities for the two derivatives in 80% Me_2SO and eventually to a significantly greater acidity of **5d** ($\Delta pKa \sim 2.8$) in pure Me_2SO. Similar inversions occur between nitromethane **4** and all the benzyltriflones **5a–e**, for example.

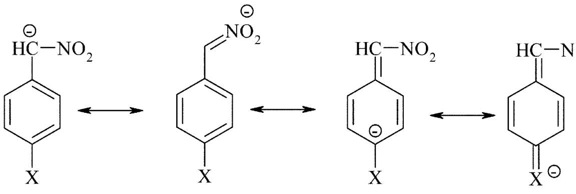
NMR evidence. As is borne out by the results in Table 1, the ionization of phenylnitromethane **6a** is accompanied by large downfield shifts of the exocyclic H_α and C_α atoms: ΔδHα = 0.99 ppm; ΔδCα = 29.90 ppm in Me_2SO solution.[26] At the same time, the ionization induces a $\Delta\delta C_4$ value of −9.48 ppm, which is much lower than expected for maximum charge delocalisation onto the *para* carbon of a phenyl ring ($\Delta\delta C_4 \sim -25$ ppm).[33] These results are fully consistent with only a minor con-

Table 3 p*K*a values for 4-X-substituted benzyltriflones **5a**–**e** and related carbon acids in H_2O, Me_2SO and various H_2O–Me_2SO mixtures[a]

								Me_2SO	
Structure	X	Compound	H_2O	30% Me_2SO	50% Me_2SO	70% Me_2SO	90% Me_2SO	p*K*a	λ_{max}/nm
	H	**5a**[b]	—	—	15.10	14.80	—	14.62	290
	CF_3	**5b**	—	13.82	13.30	—	—	11.95	316
	CN	**5c**	—	12.82	12.00	11.02	—	10.70[c]	347[d]
	NO_2	**5d**[b]	—	11.75	10.57	9.55	—	9.46	476
	SO_2CF_3	**5e**	11.60	10.65	9.77	8.67	8.21	8.85	366
	H	**6a**[e]	6.77	—	7.93	8.53	10.68	12.32(12.20)	326[f]
	NO_2	**6d**[g]	5.89	—	6.02	—	—	8.62[h]	462[f]
	NO_2	**7d**[i]	13.45	—	12.62	—	—	12.36(12.30)	515[i]
CH_3NO_2		**4**[e]	10.28	—	11.32	12.44	14.80	17.20	233[f]

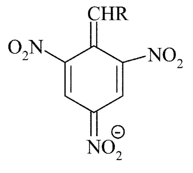
[a] T = 25 °C; [b] Ref. 20; (c) [c] Ref. 19c; [d] in 30 : 70 (v/v) H_2O–Me_2SO; [e] Ref. 24 at 20°C; [f] in 10 : 90 (v/v) H_2O–Me_2SO; [g] Ref. 25; [h] Ref. 44; [i] Ref. 24c.





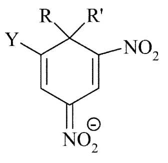
tribution of structure **6D** (X = H) to the stabilization of the conjugate carbanion **C6-a** which may actually be regarded as the nitronate ion, structure **6B**. Interestingly, there is evidence that a similar situation prevails in the case of *para*-nitrophenylnitromethane **6d** whose ionization is accompanied by similar ΔδHα and ΔδCα values, as well as a $\Delta\delta C_4$ value of −7.9 ppm for the *para* carbon bearing the NO_2 group.[25] Should this group accommodate a large portion of the negative charge of **C-6d** (structure **6E**), a much more negative Δδ value would have been expected on the basis of the numerous data documented in the literature for nitrocyclohexadienyl anions of type **C-10** or **11** (Δδ = −25 to −50 ppm).[34–39] It thus appears that the aforementioned acidifying effect of the X-substituent in the phenylnitromethane series is in fact associated with a F_π effect.[40]

Importantly, the NMR data accompanying the ionization of benzyltriflone **5a** reveal a strong upfield shift of the Hα resonance: ΔδHα = −1.87 ppm and concomitantly, the Cα resonance moves only slightly to low field : ΔδCα = 0.22 ppm. These results support the idea that most of the negative charge remains localized on the exocyclic carbon (structure **5a**) and is therefore subject to polarizability influences.[20,29–32] This is further in accord with the aforementioned finding that the acidity of **5a** becomes enhanced in Me_2SO (Fig. 2).



C-10

a) R = H
b) R = CO-CH_3
c) R = CO-C_6H_5
d) R = CO-C_6H_4-NO_2 (p)
e) R = CO-C_6H_4-OMe (p)

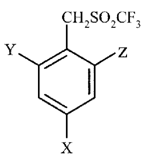


11

Y = H, CF_3, CN, NO_2
R= R' = OMe
R=H, R' = CH_2-CO-CH_3
R=H, R' = -CH(CH_3)-CO-CH_2-CH_3

As can be seen in Table 3, introduction of CF_3, CN, NO_2 and SO_2CF_3groups in the *para* position of the phenyl ring of **5a** does not change fundamentally the charge distribution, inducing only modest changes in the ΔδHα and ΔδCα values, *e.g.* ΔδHα = −1.46; ΔδCα = 11.98 ppm for X = NO_2. For comparison, extensive delocalisation of negative charge through a phenyl ring, giving rise to pure sp^2-hybridized cyclohexadienyl carbanions, *e.g.* **C-10a**–**e**, induces ΔδCα values in the range 50–60 ppm.[37–39] At the same time, the ΔδC4 value of −16.7 ppm associated with the ionization of **5d** remains very far from the

Table 4 p*K*a Values for 2,4,6-Y,X,Z-substituted benzyltriflones **9a–f** in H_2O, Me_2SO and various H_2O–Me_2SO mixtures[a]

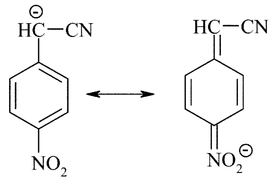
Structure	X	Y	Z	Compound	H_2O	30% Me_2SO	50% Me_2SO	70% Me_2SO	90% Me_2SO	Me_2SO	
										p*K*a	λ_{max}/nm
	CF_3	NO_2	H	**9a**	11.30	10.00	8.81	7.10	7.15	7.30	321
	NO_2	NO_2	H	**9b**[b]	—	7.98	6.94	5.61	—	5.05	433
	SO_2CF_3	NO_2	H	**9c**	7.72	6.80	5.60	4.30	3.60	3.80	355
	CF_3	NO_2	NO_2	**9d**	9.65	8.30	7.34	5.34	5.51	6.65	307
	NO_2	NO_2	NO_2	**9e**[b]	—	6.87	6.16	4.40	—	4.47	438
	SO_2CF_3	NO_2	NO_2	**9f**	6.90	5.40	4.31	2.50	2.49	2.89	404

[a] T = 25°C; [b] Ref. 20.

values reported for the accommodation of a full negative charge by a *para* nitro group (*vide supra*).[33]

Altogether, the NMR results confirm that the increase in the acidity of the benzyltriflone series on going from H_2O to Me_2SO is the reflection of a greater stabilization of the polarizable negative charge residing on Cα by the dipolar aprotic solvent. On the other hand, the acidifying effect of the 4-X substituent on the α substituent is essentially the result of a F_π type electronic effect, as it is also in the phenylnitromethane series. It follows that all resonance contributors implying charge delocalisation through the ring (structures **5D**, **5E**) or the SO_2CF_3 group (structures **5B**, **5C**) play a minor role in the stabilization of **C-5a–e**. This experimental evidence is somewhat in disagreement with recent theoretical works which have emphasized the possible role of negative hyperconjugation (drawn here as **5C**) in the stabilization of triflone carbanions.[10–13]

Electronic transmission of SO_2CF_3 *vs.* CN. The above NMR and pK_a data also emphasize that the electronic mode of action of the SO_2CF_3 group is somewhat similar to that of a CN group. As can be seen from Table 3, the effect of adding Me_2SO to an aqueous solution is to increase the acidity of *p*-nitrobenzyl cyanide **7d** in the same way as it does for triflones **5a–e**, notably the *p*-nitro substituted analogue **5d** in Fig. 2.[41] In view of the much lower electron-withdrawing effect of a CN group compared to the SO_2CF_3 group, one might argue that an activating *p*–NO_2 group will induce a greater transfer of negative charge through the phenyl ring in the case of the α-cyano carbanion **C-7d** than with the α-SO_2CF_3 carbanion **C-5d**.


7A **7E**

On this ground, the enhancing effect of Me_2SO on the acidity of **7d** could be viewed as the result of a preferential stabilization of **C-7d** through **7E** rather than **7A**. However, this explanation is not very attractive since the ionization of **7d** is found to generate a significant up-field shift of the H_α resonance ($\Delta\delta H_a$ = −0.23 ppm),[41] leaving little doubt that an appreciable portion of the negative charge must reside at the C_α carbon of **C-7d**. It follows that the enhancing effect of Me_2SO on the acidity of **7d** must be largely the reflection of an increased stabilization of structure **7A** by this dipolar aprotic solvent, in accord with the view that both α-cyano and α-SO_2R substituents derive most of their activating character from polarization effects.

Effects of modulation of the acidity of benzyltriflones by cumulative ring substitution

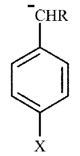
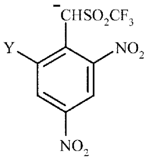
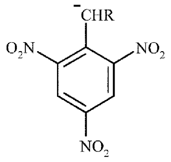
It has been shown above that monosubstitution at the *para* position, including by NO_2 and SO_2CF_3 groups, is not very effective in inducing transfer of negative charge from the exocyclic α-SO_2CF_3 substituted carbanion center to the phenyl ring. We have therefore investigated the ionization of the series of 2,4-Y,X- and 2,4,6-Y,X,Z- substituted triflones **9a–f** in a parallel study on acidity and ^1H and ^{13}C NMR shifts. As evidenced in Table 4, the acidity of these compounds is increased by 3 to 4 orders of magnitude on going from water to Me_2SO solution. This compares with two to three orders of magnitude acidity increases for the mono substituted analogues, which suggests in turn a greater importance of polarizability effects and, therefore, that polysubstitution induces a greater participation of the phenyl ring to the accommodation of negative charge.

Furthermore, Table 2 shows that the ΔδHα values associated with the ionization of **9a–f** are markedly less negative than for **5a–e**, ranging from −0.28 ppm for the 2-nitro-4-trifluoromethylbenzyltriflone **9a** to essentially zero for the 2,6-dinitro-4-trifluoromethylsulfonyl and 2,4,6-trinitrobenzyltriflones (**9f** and **9e**). This trend is in agreement with a regular increase in the contribution of the activated phenyl ring to charge delocalisation. A noteworthy feature, however, is that the above ΔδHα values remain considerably smaller than those characterizing the ionization of ring substituted toluenes which are known to afford purely sp^2 hybridized-type carbanions, as mentioned earlier.[37–39] Similar conclusions can be drawn from the $\Delta\delta C_\alpha$ values which increase from +14 to +28 ppm on going from **9a** to **9f**, while differing appreciably from the ΔδCα values associated with formation of pure sp^2-hybridized carbanions of type **C-10** (*vide supra*).[37–39]

It is interesting that the above results strongly indicate that even with multiple ring substitution, including strongly electron-withdrawing substituents like NO_2 or SO_2CF_3, most of the negative charge of the carbanions still resides in the vicinity of the exocyclic α- SO_2CF_3-substituted carbon. This remarkable predominating influence is the subject of further studies in our laboratory.

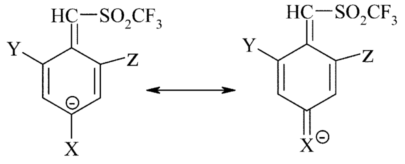
The ^{13}C NMR results call for an additional remark concerning the relative capabilities of the NO_2 and SO_2CF_3 groups to delocalize negative charge by resonance. With reference to contributions such as **9D** and **9E** to charge transfer in the phenyl ring, it is noteworthy that ionization of the related 4-SO_2CF_3 and 4-NO_2-substituted triflones always results in a greater shielding of the C_4 carbon bearing a SO_2CF_3 group: *e.g.* $\Delta\delta C_4$ = −21.89 ppm and $\Delta\delta C_4$ = −27.1 ppm for the triflones **9c** and **9f**, as compared with $\Delta\delta C_4$ = −14.30 ppm and $\Delta\delta C_4$ = −18.57 ppm for the corresponding nitro compounds **9b** and **9e**, respectively. Interestingly, a similar observation can be made with respect to the contributors **5D** and **5E** for 4-X-substituted triflones : $\Delta\delta C_4$ = −20.42 ppm and −16.69 ppm for **5e** and **5d**, respectively. These data can obviously be understood in terms of the large predominance of structure **9D** (or **5D**) over **9E** (or **5E**) in the accommodation of negative charge by the SO_2CF_3 group at the *para* position of a phenyl ring, in satisfying accord with our conclusions that the preferred mode of electronic action of a SO_2CF_3 group is in terms of polarizability effects. Note that it is

Table 5 Effect of α- and ring substitution on the UV-visible absorption of some selected benzyl carbanions in Me_2SO

Structure	R	X	Y	Compound	λ_{max}/nm in Me_2SO
	H	H	—	**C-8a**	360[a]
	H	NO_2	—	**C-8d**	442[b]
	NO_2	H	—	**C-6a**	326[c]
	SO_2CF_3	H	—	**C-5a**	290[a]
	NO_2	NO_2	—	**C-6d**	462[d]
	SO_2CF_3	NO_2	—	**C-5d**	476[a]
	—	—	H	**C-9b**	433[a]
	—	—	NO_2	**C-9c**	438[a]
	H	—	—	**C-10a**	520[e,f]
	$COCH_3$	—	—	**C-10b**	491[g]
	COC_6H_5	—	—	**C-10c**	517[g]
	COC_6H_4–NO_2 (p)	—	—	**C-10d**	528[g]
	COC_6H_4–OMe (p)	—	—	**C-10**[e]	495[g]

[a] This work; [b] Ref. 41 and 42a; [c] Ref. 43; [d] Ref. 25 in 10 : 90 (v/v) H_2O–Me_2SO; [e] Ref. 46; there is a secondary maximum at 640 nm; [f] λ_{max} = 514 nm in EtOH; Ref. 45; [g] Ref. 37 in 50 : 50 (v/v) H_2O–Me_2SO.

the situation depicted in **9D** which is actually taken into account in the definition of the Hammett σ_{p-} constant of the SO_2CF_3 group.[4,6]



9D **9E**

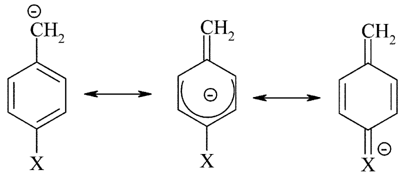
Returning to Table 4, it is worth noting that the cumulation of strong electron-withdrawing groups in the ring of benzyltriflone **5a** results in remarkably high carbon acidities with the 4-SO_2CF_3 substituted derivative being the most acidic triflone in the series, both in aqueous ($pK_a^{H_2O}$ = 6.90) and Me_2SO ($pK_a^{Me_2SO}$ = 2.89) solutions. Interestingly, the data also show that a SO_2CF_3 group is significantly more activating than a NO_2 group when it acts as a ring substituent contributing to the stabilization of a developing negative charge in a phenyl ring, in agreement with the relative σ_{p-} or σ_p values. As can be seen from a comparison of the entries **9e** and **9f**, or **9b** and **9c**, in Table 4, the effect is about 1.5 pK_a units in the present benzyltriflone series. This finding is in fair agreement with previous reports that anionic σ-adducts derived from nucleophilic addition to arenes or heteroarenes activated by SO_2CF_3 groups are in general thermodynamically more stable than their nitro analogues.[15–18]

Effect of α and ring substitution on UV-visible absorption spectra

Further confirmation of some of the above conclusions can be obtained from the UV-visible data summarized in Table 5. The following observations are noted:

(1) Considering first the benzylic anion itself (**C-8a**), it is well documented that there must be appreciable charge delocalization over the benzene ring as can be visualized in structure **8D** (which is strictly not a resonance structure).[33] It is then striking that introduction of the SO_2CF_3 group at Cα causes a hypsochromic shift to 290 nm for **C-5a** from 360 nm in **C-8a**,[41] supporting the absence of any appreciable contribution of the ring (structure **5D**) to charge delocalization in **C-5a**. A similar situation holds upon introduction of the exocyclic NO_2 group giving **C-6a**. In this instance, the absorption maximum is in fact typical of the nitronate functionality, $CH{=}NO_2^-$.[24]

(2) Proceeding to the *p*-nitro series, it is found that on going from the benzyl anion **C-8a** to the *p*-nitrosubstituted one **C-8d**, there is a bathochromic shift of ∼−80 nm which reflects the increased delocalization of charge through the *p*-nitro group relative to the benzyl anion itself (structure **8E**, X=NO_2).[41,42a]



8A 8D 8E

The situation on further introduction of the NO_2 group at Cα to give **C-6d** is made complicated by the observation of a strong solvent effect on the UV-Visible absorption of this species (λ_{max} = 380 nm in H_2O; λ_{max} = 462 nm in H_2O–Me_2SO 10–90 (v/v)).[25] This suggests that on going from hydroxylic solvents to Me_2SO media, the loss of H-bonding solvation at the Cα = NO_2^- group of **C-6d** is at least partially overcome by stabilization of polarisable negative charge at the *p*–NO_2 group.[25] In contrast, for the 4-nitrobenzyltriflone anion **C-5d**, there is almost no variation in λ_{max} with the Me_2SO content (see Table 5), showing that solvation through H-bonding does not play a major role in determining the distribution of the negative charge. The fact that the absorption maximum of **C-5d** is virtually identical to that of **C-6d** at high Me_2SO concentrations suggests that the degree of charge delocalization onto the p-nitrophenyl moiety is similar in the two cases, in accord with a predominant polarizability phenomena for the systems.

(3) Finally, the available literature data allow a comparison of the effects of picryl substitution on carbanion stabilization by α-SO_2CF_3 (carbanion **C-9e**) and α-keto groups (carbanions **C-10b–e**)[37] in the absence of data for the α-nitro analogue. Significantly, the α-keto substituted carbanions all have λ_{max} at long wavelengths (λ_{max} ∼ 510 nm), which compare well with the situation for the TNT carbanion **C-10a**.[42b,43,45,46] This has been shown to reflect an essentially complete charge delocalization through the picryl ring. In contrast, the finding of λ_{max} at

435 nm for the α-SO_2CF_3 carbanion **C-9a**, represents a marked decrease relative to **C-10a** and confirms that only modest charge transfer occurs into the picryl ring.

Conclusion

Our study has shown conclusively that the exceptional electron transmission ability of the SO_2CF_3 group in carbanion stabilization results essentially from a polarizability effect in contrast with the NO_2 group which acts largely through resonance stabilization.

As a consequence of the different modes of electronic transmission of the NO_2 and SO_2CF_3 groups, the relative electron-withdrawing effects exerted by these two substituents are particularly sensitive to the nature of the solvent when they are directly bonded to the ionisable site. Other things being equal, in benzylic systems the NO_2 group is considerably more activating than the SO_2CF_3 group in aqueous solutions where hydrogen bonding solvation of nitronate structures is favoured. Thus, the unsubstituted benzyltriflone **5a** is 7 p*K* units less acidic than phenylnitromethane **6a** in 50 : 50 (v/v) H_2O–Me_2SO. However, the acidity difference between these two substrates falls to 2 p*K* units in pure Me_2SO where stabilization of polarizable charges is favoured.

In contrast, the role of the two groups appears to be much less differentiated when they are in position of both acting through a F_π effect. This situation is here illustrated by the relatively similar acidities of both the 4-nitro and 4-SO_2CF_3-substituted benzyl triflones **5d** and **5e** over the whole range of H_2O–Me_2SO mixtures.

Experimental

Material

The synthesis of the various triflones **5a**–**e** and **9a**–**f**, either by Hendrickson's method or a new methodology, was recently reported elsewhere.[47,48]

Dimethyl sulfoxide was refluxed over calcium hydride and distilled and the fractions of 32–35 °C (under 2 mmHg) were collected and stored under nitrogen. Only freshly prepared solutions were used in the spectrophotometric studies carried out in pure Me_2SO. H_2O–Me_2SO solutions were prepared as described previously.[21]

Acidity measurements

The acidity **5a**–**e** and **9a**–**f** in the various H_2O–Me_2SO mixtures (I = 0.5 mol dm^{-3} Me_4NCl) was measured spectrophotometrically by taking into account that the conjugate carbanions exhibit a strong UV-visible absorption in regions of the spectrum where neither the parent triflones nor the required buffers absorb. These included a number of previously calibrated amine, phenol or carboxylic acid buffers that we used extensively in previous studies of the ionization of other benzylic carbon acids.[21,37] That this standard methodology applied very well to the triflones at hand is nicely illustrated by Fig. 1. λ_{max} values of **C-5a**–**e** and **C-9a**–**f** are quoted in Tables 3 and 4.

The same spectrophotometric procedure was also employed using amine buffers to measure the p*K*a values of **5b**–**e** and **9a**–**f** in pure Me_2SO. As previously reported, the $pK_a^{Me_2SO}$ of **5a** was not accessible in amine buffers.[23] In this instance, the acidity of buffers made up from **5a** itself was therefore determined with reference to appropriate indicators, *i.e.* 2,4-dinitroaniline and 4,4′-dinitrodiphenylmethane.[23] The $pK_a^{Me_2SO}$ value thus measured for **5a** (pK_a = 14.62) agrees very well with that previously reported by Bordwell (pK_a = 14.55).[49]

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