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Substituent effects on the solvolysis of 1,1-diphenyl-2,2,2-trifluoroethyl tosylates. Part III.†
Effects of electron-donating substituents in the fixed aryl moiety

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ABSTRACT: The solvolysis rates of 1-aryl-1-(*p*-methoxyphenyl)-2,2,2-trifluoroethyl and 1-aryl-1-(*p*-phenoxyphenyl)-2,2,2-trifluoroethyl bromides and chlorides were conductimetrically measured at 25.0 °C in 80% aqueous ethanol. The solvolysis rates of 1-(*p*-methylphenyl)-fixed series were also set up to analyze the substituent effect. The substituent effects on these Y-series of solvolyses were analyzed on the basis of the Yukawa–Tsuno equation. The *p*-methoxyphenyl-fixed series showed a linear correlation with $\rho = -1.7$ and $r = 1.0$ for the substituent range less reactive than *p*-Me including all *meta* substituents, and a discrete correlation with $\rho = -3.9$ and $r = 1.26$ for the strong π-donor class substituents more reactive than *p*-PhO. A similar bilinear correlation was obtained for the Y = *p*-PhO series. The partial correlations for the strong π-donor class substituents in both Y-series are nearly the same as the correlation $\rho = -4.2$ and $r = 1.2$ for symmetrically disubstituted (X = Y) series. These bilinear (or non-linear) correlations were explicable in terms of changes in the coplanarity of the two benzene rings depending upon the resonance capabilities of X and Y substituents. For strong π-donor class X substituents as strongly π-electron donating as the Y substituent, both aryl rings are equivalently twisted as in the symmetrical X = Y series, and for less electron-donating X substituents, the fixed *p*-methoxyphenyl (or *p*-phenoxyphenyl) ring remains in a coplanar conformation and X–phenyl is twisted more out of coplanarity. In the fixed Y = *p*-Me series, a significantly non-linear correlation was found, comprising three distinct correlations characteristic of three conformers, a conformer with the X–aryl coplanar and Y–aryl twisted, a symmetrical conformer with X being a weak or moderate π-electron donor and both aryls being equivalently twisted, and a conformer with Y–aryl coplanar and X–aryl twisted. The relative stabilities of these conformers were estimated by the *ab initio* MO optimization of the mono-*p*-methoxycarbenium ion, confirming the conclusions above. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: deactivated carbocationic solvolysis; substituent effect; Yukawa–Tsuno equation; varying resonance demand; loss of coplanarity; *ab initio* MO calculation

INTRODUCTION

For a variety of benzylic solvolyses, where a cationic center capable of direct π-delocalization with the benzene ring is generated, the Yukawa–Tsuno (Y–T) equation,[2]

$$\log(k/k_0) = \rho(\sigma^\circ + r\Delta\bar{\sigma}_R^+) \qquad (1)$$

is widely used in order to discuss the substituent effect in a theoretically reasonable way.[3–5] The *r* value is a parameter characteristic of a given reaction, measuring the ‘resonance demand,’ i.e. the degree of resonance interaction between the aryl group and reaction site in the transition state.[2–8] The resonance substituent parameter $\Delta\bar{\sigma}_R^+$ is defined as $\bar{\sigma}_p^+ - \sigma_p^0$.[2b,9]

By this equation, we have introduced the concept of varying resonance demand of reaction. In general applications of Eqn. (1), the *r* value has been found to vary widely from reaction to reaction, and this *r* scale permits the evaluation of the nature and structure of the transition state. In particular, the behavior of the extremely electron-deficient carbocationic systems can be characterized by extremely high *r* values. A good example is the solvolysis of the 1-phenyl-1-(trifluoromethyl)ethyl system (**1**),[8] in which the α-CF_3-induced destabilization of the carbocationic

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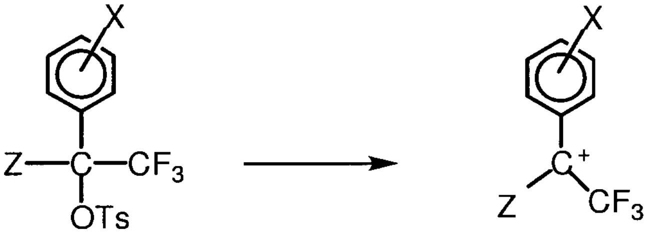


A **AC⁺**

1 $Z = CH_3$
2 $Z = H$
3 $Z = C_6H_5$; $Y = H$ in **B**
4 $Z = X\text{-}C_6H_4$; $Y = X$ in **B**

transition state provides a high resonance demand 1.39 for positive charge delocalization into the α-aryl π-system.

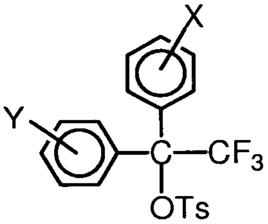
The replacement of the Z group in **A** by an aryl group provides an appropriate system **B** to reveal the substituent behavior of extremely electron-deficient carbocationic transition states. The stability of the carbocationic transition state can be widely changed by changing both the X and Y substituents in the two aryl rings, while keeping the basic framework of the structure essentially unchanged.

The substituent effects on the solvolyses of 1-(substituted phenyl)-1-phenyl-2,2,2-trifluoroethyl (**3**) and 1,1-bis(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**4**) were analyzed on the basis of the Y–T equation.[10] The symmetrically disubstituted diphenyl set **4** where X = Y gave a linear Y–T correlation [Eqn. (2)] for the whole substituent range from *p*-MeO to *m*-Cl with a high precision with $R = 0.9994$ and $SD = \pm 0.12$:

$$\log(k/k_0) = -8.30(\sigma^\circ + 1.19\Delta\bar{\sigma}_R^+)_X \qquad (2)$$

Whereas the less enhanced r value of 1.19 arises as a result of sharing the resonance demand by the two aryl groups, the ρ value, -4.15, for the effect of single aryl substituents appears appreciably smaller than that expected for an electron-deficient carbocation system.

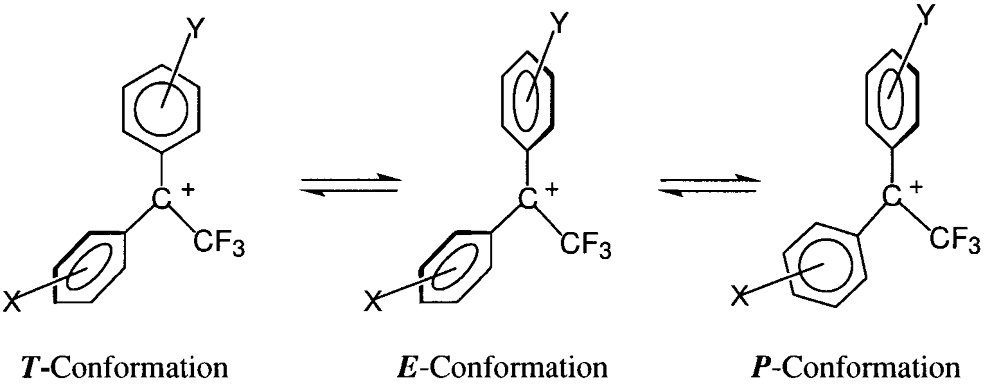
On the other hand, the monosubstituted diphenyl set **3** did not give a single linear Y–T correlation but a bilinear correlation, one with $\rho = -6.1$ and $r = 1.45$ for the substituent range more electron donating than the 3,4-dimethyl group and the other with $\rho = -4.33$ and $r = 1.26$ for the range of substituents less electron donating than the *p*-methyl group. The former correlation is comparable to those of **1** and **2**[8] and the latter to that of the symmetrically disubstituted set **4**. Since the range of



(Ts=p-$CH_3C_6H_4SO_2$)

B

5 $Y = m\text{-}Cl$
6 $Y = 3,5\text{-}Cl_2$
7 $Y = p\text{-}PhO$
8 $Y = p\text{-}CH_3O$
9 $Y = p\text{-}CH_3$



Scheme 1. Coplanarity change in 1,1-diaryl-2,2,2-trifluroethyl cation

substituent changes of reactivity in **4** entirely covers the range of reactivity change in **3**, it is highly unlikely that the non-linearity in **3** can be ascribed to the change in reaction mechanism. Nevertheless, there is obviously no simple additivity of substituent effects of the two aryl substituents in the system **B**.

Our continuing studies on this system explored the effects of the enhanced resonance demand caused by more electron-withdrawing Y substituents in the second aryl group, such as in the 1-aryl-1-(*m*-chlorophenyl)-2,2,2-trifluoroethyl (**5**) and 1-aryl-1-(3,5-dichlorophenyl)-2,2,2-trifluoroethyl (**6**) sets.[1] The behavior of **5** is

Table 1. Solvolysis rates of 1,1-diaryl-2,2,2-trifluoroethyl bromides and chlorides in 80% aqueous ethanol

Substituents		$10^5 k_t$ (s^{-1}) at 25 °C	
X_1	X_2	Bromides	Chlorides
p-MeO	*p*-OCH_2CH_2-*m*		3050[a]
	p-MeO		646.8
	p-MeS		173.7
	p-PhO	3210[a]	63.3[a]
	p-MeO-*m*-Cl		39.28, 39.3[b]
	p-MeS-*m*-Cl		16.33
	p-Me		23.5[b]
	m-Me		9.60[b]
	p-F		9.824
	H	466.6	7.504, 7.64[b]
	m-CF_3		0.890[b]
	p-CF_3		1.19[b]
p-PhO	*p*-MeS		17.51
	p-PhO	184.3, 170[a]	3.809, 3.19[a]
	p-MeO-*m*-Cl		1.830
	p-MeS-*m*-Cl		0.5969
	3,4-Me_2		0.6720
	p-Me	23.0[a]	0.425[a]
	m-Me	6.88[a]	0.140[a]
	p-F		0.1297,[c] 1.465 (at 45 °C), 33.02 (at 75 °C)
	H	5.267, 5.38[a]	0.114[a]
	m-MeO	4.19[a]	0.0824[a]
	m-CF_3	0.406[a]	0.0106[a]
	p-CF_3	0.520[a]	0.0142[a]
p-Me	*p*-OCH_2CH_2-*m*		349[a]
	p-MeS		4.989, 49.25 (at 45 °C)
	p-MeO-*m*-Cl		0.2393
	p-MeS-*m*-Cl		0.07919,[c] 0.9549 (at 45 °C), 23.39 (at 75 °C)
	p-*t*-Bu	0.2743,[c] 3.669 (at 45 °C), 102.7 (at 75 °C)	
	3,5-Me_2	0.08519,[c] 1.229 (at 45 °C), 37.89 (at 75 °C)	

[a] Ref. 11.
[b] Ref. 12.
[c] Calculated from other temperatures.

Table 2. Estimated solvolysis rates of 1,1-diaryl-2,2,2-trifluoroethyl tosylates in 80% aqueous ethanol at 25 °C[a]

Substituent	k_t (s^{-1}) at 25 °C		
X	**8**, Y = *p*-MeO	**7**, Y = *p*-PhO	**9**, Y = *p*-Me
p-OCH_2CH_2-*m*	626000[b]		80140[b]
p-MeO	132800[c]	13620[b]	5225[d]
p-MeS	36520	3681	1145
p-PhO	13620[b]	781.9[c]	97.59[b]
p-MeO-*m*-Cl	8316	375.7	54.95
p-MeS-*m*-Cl	3573	137.1	18.18
3,4-Me_2		154.3	
p-Me	5225[d]	97.59[b]	1.647[c]
p-*t*-Bu			1.164
3,5-Me_2			0.3615
p-F	2228[d]	27.04	
m-Me	2182	29.19[b]	0.1818[c]
H	1980[c]	22.35[c]	0.08046[c]
m-MeO		17.78[b]	
p-Cl			0.05481[f]
m-Cl	392.6[e]	3.175[e]	0.006234[e,f]
m-CF_3	230.7[d]	2.078[b]	
p-CF_3	308.4[d]	2.784[b]	
3,5-Cl_2	104.7[e]	0.8432[e]	0.0007194[e,f]

[a] Estimated from bromide reactivities in Table 1 based on a tosylate/bromide ratio of 4.243×10^5 for **4** (3,5-Me_2) and estimated from chloride reactivities in Table 1 based on an OTs/Cl ratio of 2.053×10^7 for **4** (*p*-PhO) as reported in Ref. 10 or an appropriate estimation based on the logarithmic linear relations of bromide–chloride reactivities in Table 1.
[b] Estimated from rate data reported in Ref. 11.
[c] Reported in Ref. 10.
[d] Estimated from rate data reported in Ref. 12.
[e] Reported in Ref. 1.
[f] Tosylate rate constant.

also similar to that of the monosubstituted set **3**, but **6** with Y = 3,5-Cl_2 only shows a normal substituent behavior, i.e. giving a linear Y–T correlation with $\rho = -6.0$ and $r = 1.69$.

In the α,α-diarylcarbocation system **BC**$^+$, the resonance demand parameter *r* should be effectively controlled by the loss of coplanarity of both p-orbitals as depicted in Scheme 1.

The molecule adopts a propeller-shaped twisted conformation due to steric repulsion, and the twist angle should be a minimum to favor the positive charge delocalization into the ring. The linear Y–T correlation for **4** leads to the conclusion that the two aryl rings in the **4** cation (**4C**$^+$) should be at least conceptually equivalent with respect to the propeller conformation.[10] For unsymmetrically substituted diarylcarbocations **BC**$^+$, the propeller shape is destroyed and the deviation from coplanarity of rings is related to the relative capabilities of resonance stabilization (mainly π-delocalization) by both aryl rings.[1,10] In **7** and **8** where a strong π-electron-donating Y substituent is introduced in to a benzene ring, only the ring having strong π-electron-donating X substituents (of the same resonance class as the fixed Y substituent) has the propeller conformation, but the Y–phenyl retains coplanarity with the carbocation center when the variable X substituents are less electron donating than the fixed Y.

In order to discuss the precise dependence of resonance demand on the aryl coplanarity, it is necessary to gather more complete set of substituent effect data for a wider range of fixed Y substituents of this solvolysis system. Consequently, we have further extended our investigation to the substituent effects on the solvolyses of 1-aryl-1-(*p*-phenoxyphenyl)-2,2,2-trifluoroethyl (**7**) and 1-aryl-1-(*p*-methoxyphenyl)-2,2,2-trifluoroethyl (**8**) sets where a strong π-electron-donating Y substituent will reduce the resonance demand of the system and in particular will affect the non-linearity of the correlation in a different way.

The substituent effects on the solvolyses of these sets are treated with the Y–T equation and the correlation results are discussed based on the dependence upon varying coplanarity of the respective benzene rings.

RESULTS AND TREATMENT OF DATA

Solvolysis data sets

Rate constants for solvolyses of the title compounds **B**, mainly **7, 8** and **9**, with a fixed Y = *p*-PhO, *p*-MeO and *p*-Me, respectively, were measured conductimetrically by using the chlorides, bromides and/or tosylates in 80% (v/v) aqueous ethanol (80E) at initial concentrations of ca

Table 3. Correlation analyses of substituent effects[a]

Entry	Substrate: (Z)[c] in **A**	n[d]	Yukawa–Tsuno equation				Brown $\rho^+\sigma^+$ equation[b]		
			ρ	r	R	SD	ρ^+	R	SD
1	**1** (CH_3)	28	-6.29 ± 0.05	1.39 ± 0.02	0.9998	$\pm$ 0.07	-7.54 ± 0.21	0.990	$\pm$ 0.49
2	**2** (H)	17	-6.05 ± 0.19	1.53 ± 0.07	0.998	$\pm$ 0.15	-8.27 ± 0.91	0.921	$\pm$ 0.85
3	**3** (Ph)	18	-4.37 ± 0.21	1.67 ± 0.13	0.996	$\pm$ 0.24	-5.93 ± 0.33	0.976	$\pm$ 0.60
4	**4** (X-Ph)	14	-4.15 ± 0.08[e]	1.19 ± 0.04	0.9994	$\pm$ 0.12	-4.74 ± 0.14	0.995	$\pm$ 0.33
5	**5** (3-Cl-Ph)	13	-5.32 ± 0.32	1.65 ± 0.14	0.997	$\pm$ 0.22	-7.93 ± 0.61	0.969	$\pm$ 0.71
6	**6** (3,5-Cl_2Ph)	13	-5.95 ± 0.31	1.69 ± 0.12	0.998	$\pm$ 0.18	-9.59 ± 0.87	0.958	$\pm$ 0.82
7	**7** (*p*-PhOPh)	15	-2.22 ± 0.24	1.29 ± 0.23	0.983	$\pm$ 0.24	-2.59 ± 0.15	0.978	$\pm$ 0.26
8	**7** (*p*-PhOPh)[f]	8	-1.86 ± 0.39	1.76 ± 0.55	0.987	$\pm$ 0.24	-2.64 ± 0.26	0.972	$\pm$ 0.32
9	**8** (*p*-MeOPh)	14	-2.15 ± 0.29	0.88 ± 0.24	0.973	$\pm$ 0.27	-2.00 ± 0.14	0.972	$\pm$ 0.26
10	**9** (*p*-MePh)	14	-3.76 ± 0.40	1.54 ± 0.25	0.988	$\pm$ 0.39	-4.98 ± 0.35	0.972	$\pm$ 0.56

[a] Substituent parameters $\sigma°$, $\Delta\bar{\sigma}_R^+$and σ^+, employed in the present analysis are mostly the standard values except for the correction of 0.03–0.04 σ unit for the resonance parameters of *p*-MeS derivatives characteristics of highly electron-deficient systems.[1,8,10]

[b] $r = 1.00$ in the Y–T equation.

[c] Z in XPhC(Z)CF_3OTs (**A**).

[d] Number of substituents involved.

[e] For two identical substituents.

[f] Data set from Liu *et al.* in Ref. 11

10^{-4} mol dm^{-3} of substrates under the same conditions as those for **3–6** in previous papers (Table 1).[1,10] Several related data available in the literature[11,12] are also included in the present analysis. Including the rate data for X = *p*-Me derivatives in all the Y sets, we have composed a new series 1-aryl-1-(*p*-methylphenyl)-2,2,2-trifluoroethyl (**9**) of Y = *p*-CH_3 by determining some additional rate data (Table 1). The rates of the halide solvolyses were converted into the rates for the corresponding tosylates on the basis of the tosylate/bromide rate ratio = 4.24×10^5 calculated from the data obtained for the 3,5-dimethyl derivative of **4** and the bromide/chloride rate ratio = 48.4 obtained for the *p*-phenoxy derivative of **4**[10] or an appropriate estimation based on the logarithmic linear relations of the bromide–chloride reactivities in Table 1. Rate constants thus estimated for the tosylate solvolysis at 25 °C for the series **7, 8** and **9** with Y = *p*-PhO, *p*-MeO and *p*-CH_3, respectively, are summarized in Table 2.

As shown in Table 2, the magnitude of reactivity change caused by the substituent change from *p*-methoxy to 3,5-dichloro in fixed Y sets, **9, 7** and **8**, varies substantially as 7.3×10^6, 1.6×10^4 and 1.3×10^3, respectively, in 80E at 25 °C. Nevertheless, these reactivity changes are significantly smaller than the corresponding coverage in the other fixed Y sets **3–6**.

Analysis of substituent effects

Detailed correlation analysis of the substituent effects based on the Y–T equation [Eqn. (1)] has been carried out for the fixed Y sets, **7, 8** and **9**, and the closely related systems reported previously, sets **3–5**[1,10] in series **B** and also **1** and **2**[8] in the series **A**. For comparison, the same analysis has also been applied separately to Liu *et al.*'s data[11] set for **7**. All the correlations are compared with those of the Brown $\rho^+\sigma^+$ analysis,[9] as summarized also in Table 3.

Sets **1** and **2** in the series **A** have already been shown to satisfy the Y–T equation with excellent precision; the correlations with Eqn. (1) are far more precise than those with the Brown equation.[8] In the series **B**, symmetrically disubstituted set **4** where X = Y gives an excellent linear correlation for the whole range of substituents over a reactivity change of 11 log units. Whereas the Y–T equation improves the correlations for all the systems included in this study, it appears to give less satisfactory linear whole-substituent correlations for any fixed Y sets where X ≠ Y in the **B** series. Nevertheless, it is apparent in Table 3 that the ρ value changes significantly with fixed substituents Y and that there is a qualitative trend of an inverse-linear change of ρ against electron-donating powers, e.g. σ^+, of Y; a similar trend can be observed also in the ρ^+ values of the Brown correlations for the series **B**. The substituent effects of X and Y in the diaryl series **B** (X ≠ Y) are all apparently non-additive. The mode of change of ρ values is in line with what would be expected from the reactivity selectivity relationship,[13,14] which is intimately related to the Hammond–Leffler rate–equilibrium relationship (or extended Brønsted relationship)[15] concerning the transition state coordinate. This is not consistent, however, with the excellent linearity of the Y–T correlation for **4** (X = Y) or with the precise additivity only in this symmetrical system. It is therefore remarkable that the Y–T equation does not correlate so precisely the substituent effects of any sets (entries 3,5 and 7–10 in Table 3) in the unsymmetrical series **B** (X ≠ Y). Indeed, the Y–T correlations for the whole range of substituents for the diaryl **B** (X ≠ Y) series are all obviously non-linear

Table 4. Correlation analyses of substituent effects[a]

Entry	Substrate (Y) in **B**	Substituents X				Yukawa–Tsuno equation		
		Substituent range	Class[b]	n[c]	ρ	r	R	SD
1	**3** (H)	p-MeO–3,4-Me$_2$	s-ED	6	-6.08 ± 0.42	1.45 ± 0.17	0.996	± 0.12
2		p-MeO–3,5-Cl$_2$	w-ED,EW	12	-4.33 ± 0.08	1.26 ± 0.08	0.9990	± 0.07
3	**4** (X = Y)	p-MeO–m-Cl	whole	14	-4.15 ± 0.08	1.19 ± 0.04	0.9994	± 0.12
4	**5** (3-Cl)	p-MeO–p-Me	s-ED	7	-6.19 ± 0.52	1.57 ± 0.20	0.996	± 0.19
5		3,5-Me$_2$–m-Cl	w-ED	6	-4.81 ± 0.11	1.41 ± 0.08	0.9993	± 0.05
6	**6** (3,5-Cl$_2$)	p-MeO–p-Cl	s,w-ED	13	-5.95 ± 0.31	1.69 ± 0.12	0.998	± 0.18
7	**7** (p-PhO)	p-MeO–p-MeS-m-Cl[d]	s-ED	7	-4.01 ± 0.23	1.26 ± 0.11	0.998	± 0.10
8		p-Me–3,5-Cl$_2$	w-ED,EW	8	-2.04 ± 0.02	1.07 ± 0.05	0.9998	± 0.02
9	**8** (p-MeO)	p-Coumar[e]–p-PhO	s-ED	6	-3.94 ± 0.37	1.26 ± 0.15	0.9992	± 0.09
10		p-Me–3,5-Cl$_2$	w-ED,EW	7	-1.71 ± 0.08	1.01 ± 0.19	0.997	± 0.06
11	**9** (p-Me)	p-Coumar[e]–p-MeO-m-Cl	s-ED	5	-6.26 ± 0.34	1.40 ± 0.23	0.999	± 0.10
12		p-Me–p-Cl	w-ED	6	-3.66 ± 0.24	1.21 ± 0.20	0.994	± 0.08
13		H–3,5-Cl$_2$	EW	4	-2.91 ± 0.08		0.999	± 0.05

[a] See footnote a in Table 3.
[b] The substituent resonance class to which the substituents included in the correlation are referred (see text).
[c] Number of substituents involved.
[d] Including the points of H and p-Me estimated for the *E*-conformers (see text).
[e] XPh = 2,3-dihydrobenzofuranyl in **B**.

or bilinear. Partial correlations for limited ranges of substituents of respective Y sets are summarized in Table 4.

The whole-substituent correlation for **7** where Y = p-PhO (either entry 7 or 8 in Table 3) may be an example of poor conformity to Eqn. (1), as shown by the Y–T plot in Fig. 1. All the plots against σ^+ (open circles) of *para* π-donor substituents deviate significantly in the direction of rate enhancement from the ρ_m correlation line of $\rho = -2.04$. For the range of substituents less reactive than p-Me, i.e. weak electron-donating class substituents (abbreviated to w-ED class substituents), a precise Y–T correlation is obtained ($r = 1.07 \pm 0.05$; entry 8 in Table 4) with ρ_{YT} essentially identical with ρ_m. Since the coplanarity of aryl rings in the propeller conformation of the transition state should be determined mainly by the resonance capabilities rather than polarities of aryl substituents, we almost always observe a non-linear behavior in the substituent–reactivity correlation attributable to distinctly different contributions from the different resonance classes of substituents, strongly electron-donating substituents by resonance (denoted s-ED class), weakly or moderately electron-donating substituents (denoted w-ED class) and electron-withdrawing substituents (denoted EW class). Thus, not only for qualitative interpretations but also for the practical purpose of correlational treatments, the substituents involved in the present study are classified to define explicitly three different resonance classes substituents: s-ED class, p-OCH$_2$CH$_2$-m-, p-MeO, p-MeS, p-PhO, p-MeO-m-Cl and p-MeS-m-Cl, having $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$values of – 0.6 to – 0.75; w-ED class, p-Me, comparable p-alkyls, 3,4-Me$_2$ and p-halogens, and including 3,5-Me$_2$, m-Me and H; EW class, m-halogens, m- and p-CF$_3$ and more strongly EW substituents. On the other hand, a separate Y–T correlation (entry 7 in Table 4) with $\rho = -4.0$ is obtained for more electron-donating substituents than p-MeS-m-Cl, i.e. strong electron-donating resonance class substituents (abbreviated to s-ED class substituents) (see note in brackets above). The r value of the Y–T

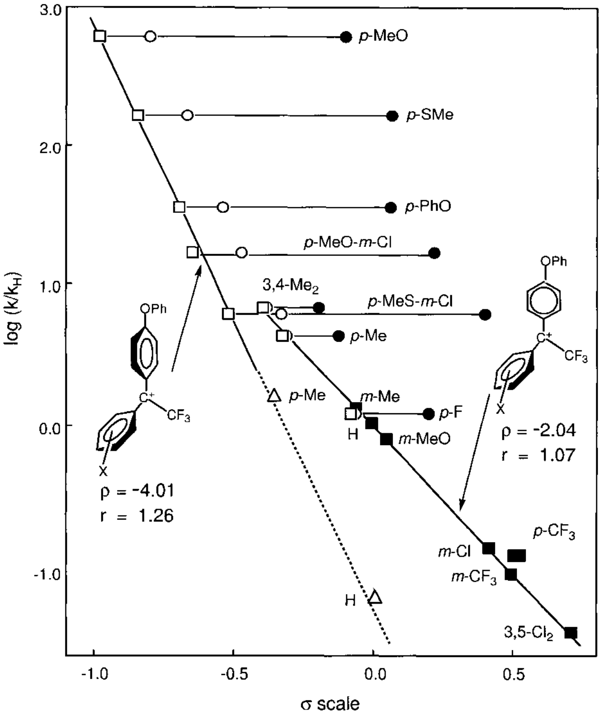


Figure 1. Y–T plot for solvolysis of 1-(p-phenoxyphenyl)-1-(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**7**) in 80% aqueous EtOH at 25.0 °C: ○, σ^+; ●, σ^0; □, $\bar{\sigma}$ ($r = 1.26$ for strong p-π-donors and $r = 1.07$ for weak ones); ■, σ^0 for resonance invariant substituents

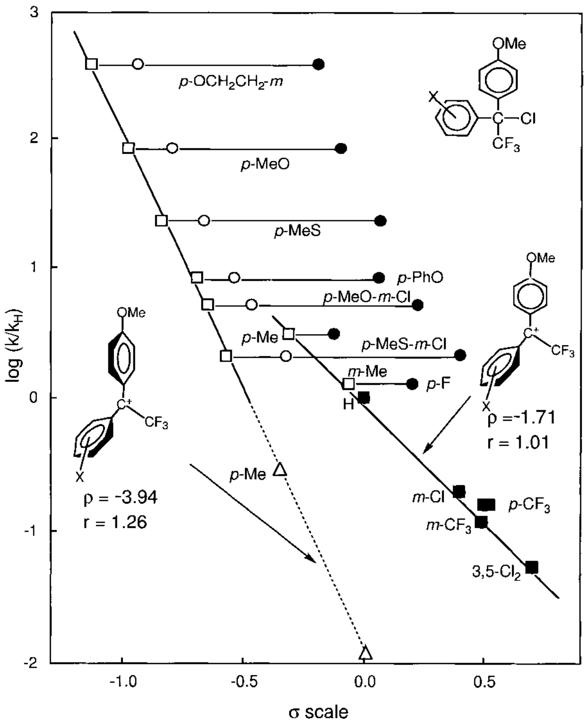


Figure 2. Y–T plot for solvolysis of 1-(p-methoxyphenyl)-1-(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**8**) in 80% aqueous EtOH at 25.0 °C: ○, σ^+; ●, σ^0; □, $\bar{\sigma}$ ($r = 1.26$ for strong p–π donors and $r = 1.0$ for weak ones); ■, σ^0 for resonance invariant substituents

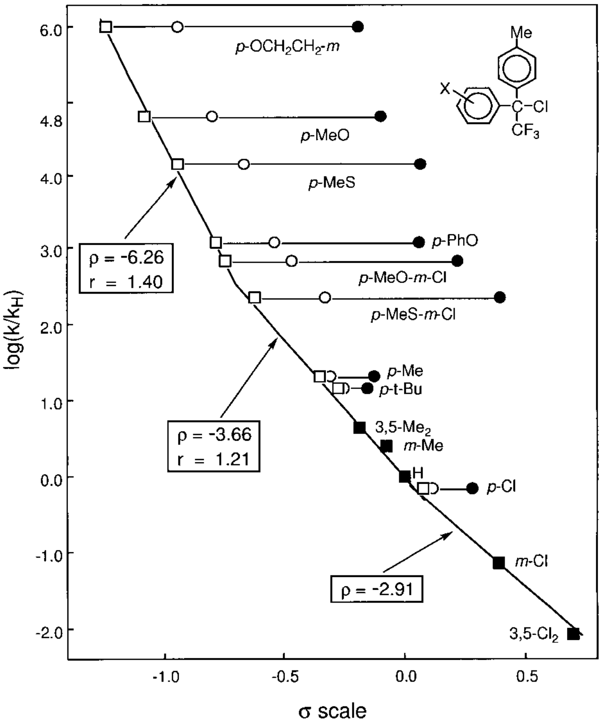


Figure 3. Y–T plot for solvolysis of 1-(p-methylphenyl)-1-(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**9**) in 80% aqueous EtOH at 25.0 °C: ○, σ^+; ●, σ^0; □, $\bar{\sigma}$ ($r = 1.4$ for strong p–π-donors and $r = 1.2$ for weak ones); ■, σ^0 for resonance invariant substituents

correlation appears to be difficult to determine directly from the substituent reactivity data available and this will be considered later in detail.

Similarly, the Y–T equation fails to correlate the substituent effect on the solvolysis of **8** where $Y = p$-MeO (entry 9 in Table 3), resulting in a bilinear correlation as in Fig. 2, which comprises a correlation (entry 9 in Table 4) with $\rho = -3.9$ and $r = 1.26$ for strongly electron-donating resonance class substituents and another separate correlation (entry 10 in Table 4) with $\rho \approx -1.7$ for the range of substituents less electron donating than the p-methyl group, i.e. for w-ED and EW groups (see note in brackets above). Highly important, both sets **7** and **8** indicate clearly bilinear Y–T correlations with a higher ρ value for the substituent range accelerating reactivity and with a significantly lower ρ value for the range of reducing reactivity. This may imply an anti-Hammond shift of the transition state coordinate and is not altogether consistent with what has been concluded above (in Table 3) from the behavior of ρ in the whole-substituent correlations in the series **B** ($X \neq Y$).

The behavior of substituents in the solvolysis of **9** where $Y = p{-}CH_3$ is illustrated by the Y–T plot in Fig. 3.

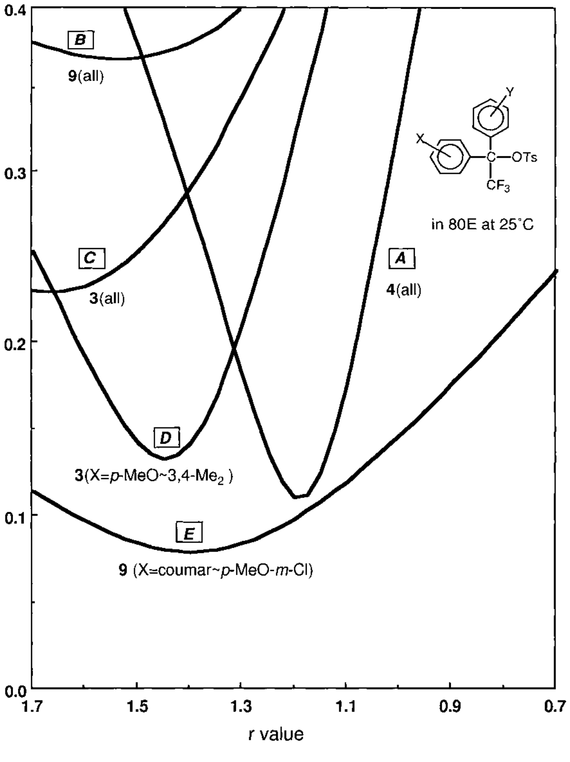


Figure 4. Plot of standard deviations as a function of r values for the solvolysis; A for 1,1-bisaryl-2,2,2-trifluoroethyl tosylates (**4**), C for all substituents and D for the range of substituents X = p-MeO–3,4-Me$_2$ of monosubstituted 1,1-diphenyl-2,2,2-trifluoroethyl tosylates (**3**), and B for all substituents and **E** for the range of substituents X = coumaranyl–p-MeO-m-Cl of 1-(p-methylphenyl)-1-(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**9**) in 80% aqueous EtOH at 25.0 °C

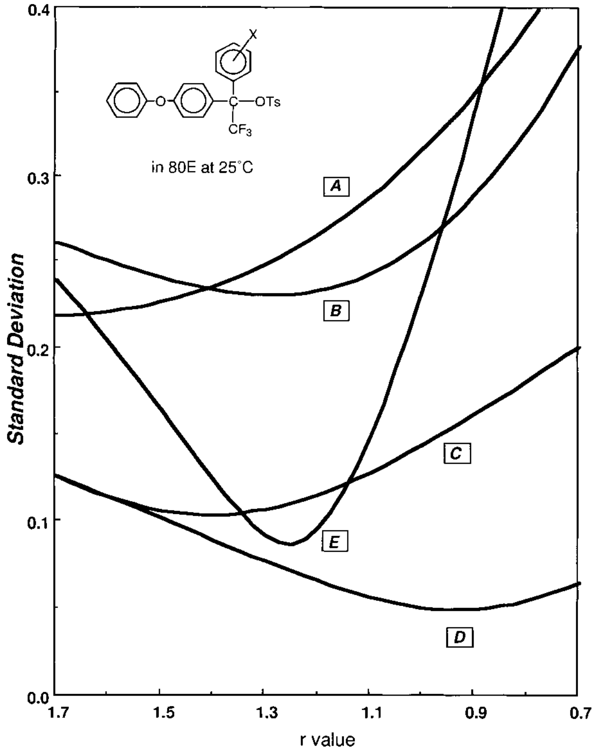


Figure 5. Plot of standard deviations as a function of *r* values for the solvolysis of 1-(*p*-phenoxyphenyl)-1-(substituted phenyl)-2,2,2-trifluoroethyl tosylates (**7**) in 80% aqueous EtOH at 25.0 °C. A for Liu *et al.*'s set of **7** (entry 8 in Table 3); B for all substituents set of **7** (entry 7 in Table 3); C for set of s-ED of **7**; **D** for set of **7** without s-ED substituents; E for s-ED substituents including the points estimated for *p*-Me and H

It is apparent that the effects of whole range substituents are not linearly correlated with σ^+ parameters; the σ^+ points (open circles) of *para* π-donor substituents show a significant concave plot, exhibiting significant deviations in the direction of rate enhancement from the reference correlation line. The solvolysis of **9** does not appear to adopt a single linear Y–T correlation with an *r* value for the whole range of substituents.

The quality of Y–T correlations can be discussed most reasonably on the basis of the relation between standard deviations (SD) and varying *r* values. In Fig. 4, the SD vs *r* correlation curves are displayed for the solvolysis of **3** where Y = H and **9** where $Y = p{-}CH_3$, compared with that for **4** where X = Y as a reference. Curve *A* for **4** is typical of the satisfactory Y–T correlations of acceptable conformity; both the depth (at the minimum SD point) and the steepness of the wedge-shaped plot are important indices to qualify the Y–T correlation (actually to evaluate the resonance demand *r* value). From the significant difference >0.2 in SD between the minimum SD and that at *r* = 1.0 for curve *A* in this plot, an *r* value of 1.19 assigned for this set **4** can be distinguished from a constant *r* of unity assumed in the Brown $\rho^+\sigma^+$ equation. In contrast, the SD vs *r* curve *B* for all the substrates of the set **9** results in neither a sufficient depth of the best-fit SD nor a sharp wedge shape plot of the curve, and is similar to curve *C* for the monosubstituted set **3** where Y = H. This flat curve of insufficient depth of SD >0.2 should be incapable of discriminating the change in *r* value of the sets. Deleting the X substituents more electron withdrawing than H brings about a small improvement in the sharpness of the wedge-shaped curve, and further deleting less electron-donating substituents than *p*-methyl results in a significant improvement in the depth of the SD vs *r* curve *D* to reach a satisfactory precision level of acceptable conformity to Eqn. (1) (cf. entry 1 in Table 4).

Figure 5 displays the SD vs *r* relationships of the partial Y–T correlations for ranges of X substituents of **7** (Y = *p*-PhO). Curves *A* and *B* exhibit a behavior of the SD for the whole-substituent correlations of Liu *et al.*'s data set (cf. entry 8 in Table 3) and of our whole-substituent set of **7** (cf. entry 7 in Table 3), respectively; the two sets differ in the number of substituents involved but cover a comparable range of substituents from *p*-MeO to p-CF_3 or 3,5-Cl_2. Both *A* and *B* represent similar broad curves of comparable low precision, SD $\geq$0.2, and there is no significant convergence to any *r* value. While Liu *et al.*[11] stressed to the fact that the Y–T correlation with *r* = 1.76 obtained for **7** gave a small improvement in the linearity compared with the Brown σ^+, the data set **7** itself does not seem appropriate for the purpose of discussing the predictability of the two equations. The SD level $\geq$0.2 implies that the system does not follow a single substituent interaction mechanism throughout the range of substituents; the best-fit *r* value for the whole-substituent set does not have any mechanistic significance. The set of s-ED class substituents of **7** gives curve *C* of sufficient depth with reduced SD $\leq$0.1 but still of a broad basis without significant convergence. Because of the nearly constant $\Delta\bar{\sigma}_R^+$ values within -0.60 to -0.75 for the s-ED substituents, the best-fit *r* value for the correlation of this set of s-ED substituents should be almost indefinite and consequently the points expected for H and *p*-methyl groups of different $\Delta\bar{\sigma}_R^+$values must be included in the correlation in order to attain a sufficient depth in the SD vs *r* curve for this resonance class of substituents (curve *E*). For the range of substituents besides the s-ED class we can observe a precise best-fit Y–T correlation with SD $\ll$ 0.1, irrespective of a conceivable change in *r* value (curve *D*). The SD vs *r* relationship for the set **8** where $Y = p{-}MeO$ behaves in a similar manner to that for the set **7** where $Y = p{-}PhO$.

It should also be noted that the Y–T correlation for any set of substituents in the same resonance class should statistically give precisely a constant ρ value while the *r* value is almost indefinite. For example, in the set of s-ED class substituents having nearly the same $\Delta\bar{\sigma}_R^+$values, the

ρ value should be related almost exclusively to their varying $\sigma°$ values, independent of the r value. The symmetrical X = Y members, X = *p*-MeO, *p*-PhO, and *p*-Me, in the sets, **7, 8** and **9**, respectively, should of course satisfy the Y–T correlation in Eqn. (2) defined by the set **4** (entry 4 in Table 3) and, moreover, X substituents in the same resonance class with fixed Y in any set appear altogether to satisfy the same Y–T correlation in Eqn. (3) as for set **4**. For substrates where the two aryl substituents X and Y are in the same resonance class having identical $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$values and symmetrical substrates where X = Y, a precise additivity relationship holds with excellent precision, $n = 24$, SD = ±0.126 and $R = 0.9992$;

$$\log(k/k_0) = -(4.143 \pm 0.077)(\bar{\sigma}_{\mathrm{X}} + \bar{\sigma}_{\mathrm{Y}}) \qquad (3)$$

where

$$= -(4.143 \pm 0.077)\{(\sigma^{\circ}_{\mathrm{X}} + \sigma^{\circ}_{\mathrm{Y}}) + (1.200 \pm 0.033)[(\Delta\bar{\sigma}_{\mathrm{R}}^{+})_{\mathrm{X}} + (\Delta\bar{\sigma}_{\mathrm{R}}^{+})_{\mathrm{Y}}]\}$$

The r and ρ values for such correlations (entries 2, 7, 9 and 12 in Table 4) for the respective Y sets all coincide with those of the correlation in Eqn. (3). While we should generally take into account the relatively low confidence in the precision of the partial correlations, they can be most likely all be replaced by the r and ρ of the correlation in Eqn. (3).

In the case of the set **7**, as seen in Fig. 1, the correlation for s-ED class substituents is indeed statistically indefinite especially with respect to the r value, and the correlation for this class of substituents (plotted as open squares in Fig. 1) can be confirmed with the aid of Eqn. (3). The log k_{H} value expected for the unsubstituted member (X = H) of the equivalent diaryl substituents series in **7** can be estimated as (half) of log $(k/k_0)_{\mathbf{4}}$ for the substrate X = *p*-PhO in **4** (X = Y); the same estimation applies also to the log (k/k_0) of the X = *p*-Me member of the same series. The Y–T correlation (entry 7 in Table 4) was obtained based on these s-ED class substituents especially including these two estimated points (plotted as open triangles in Fig. 1); the whole Y–T plot is determined as in Fig. 1.

Similarly, plots of log $(k/k_0)_{\mathbf{8}}$ values for **8** with Y = *p*-MeO also fall on the correlation line [Eqn. (3)] only for the s-ED class substituents; w-ED (resonance) class substrates show a clear break of the Y–T correlation (Fig. 2).

Here we note our conclusion that not only the Brown equation but also the Y–T equation should be incapable of correlating the effect of the whole range of X substituents in any fixed Y set, except for **4** where Y = X, as a single linear correlation of acceptable conformity. However, this is not caused from a deficiency of the Y–T equation but from the inadequacy of the substituent effects in the α, α-diaryl system **B** to deal with the ordinary correlation analysis. Whereas the Y–T equation fails to delineate the substituent effects in these **B** series, the equation is capable of detecting the break of the linear substituent effect correlations in the α,α-diaryl series **B**. The precision criterion for acceptable conformity of Y–T correlations should be set at much more precise SD level than that for the Brown correlations, so that the latter correlation was capable of predicting whether any rate as reasonable but incapable of detecting the non-linearity of substituent effect in the system. Indeed, the significant non-linearity in the respective Y sets is a very important result from this correlation analysis.

Conformation of carbocations

The geometries of carbocations $\mathbf{BC}^{+}$ in the α,α-diaryl system **B**, the parent carbocation $\mathbf{3C}^{+}$(H), its mono-*p*-methoxy $\mathbf{3C}^{+}$(*p*-MeO) and mono-*m*-chloro derivatives $\mathbf{3C}^{+}$(*m*-Cl) and the symmetrical di-*p*-methoxy $\mathbf{4C}^{+}$(*p*-MeO) and di-*m*-chloro derivatives $\mathbf{4C}^{+}$(*m*-Cl), were initially examined with *ab initio* MO calculations at the RHF/3–21G level. The minimum energy conformations were refined at the 6–31G* level and the potential energies associated with rotations about the $\mathrm{C_{Ar}}$—C^{+} bonds of carbocations were also evaluated at the 6–31G* level. The results of *ab initio* MO optimization were reported in part in the previous paper.[1] Optimization at the MP2/6–31G* level was carried out on several typical carbocations. The results of these calculations are summarized in Table 5 and the geometries of optimized structures located at the 6–31G* level are presented in Fig. 6.

In these optimized structures, the two phenyls of the parent carbocation $\mathbf{3C}^{+}$(H) are rotated by 19° and 41° from coplanarity with the sp^2 carbocation center. Essentially the same geometries and energetics of the optimized conformers are obtained for all other symmetrically disubstituted carbocations $\mathbf{4C}^{+}$ with X = *p*-MeO, *p*-Me and *m*-Cl. There is an appreciable non-equivalence in the twist angles between the two propeller aryls in the optimized structure of symmetrical $\mathbf{4C}^{+}$ (Y = X); this non-equivalence should be due to the non-equivalent proximity effects of the non-spherical $\mathrm{CF_3}$ group. However, the optimized structure at higher level results in a pair of much closer rotation angles, 23° and 38° [$\mathbf{3C}^{+}$(H); MP2/6–31G*]; the stability of the optimized conformer is not much different [within 0.9 kcal mol^{-1} (1 kcal = 4.184 kJ)] from that of the equivalent propeller conformation both twisted by a 23–38° (ca 30°) rotation (cf. Table 5).

On the other hand, the optimized structure of the mono-*p*-methoxy-substituted ion $\mathbf{3C}^{+}$ (*p*-MeO) in Fig. 6 has a conformation in which the phenyl ring is twisted by $\theta_{\mathrm{H}} = 53°$ whereas the *p*-methoxyphenyl is coplanar (by $\theta_{p-\mathrm{MeO}} = 8°$) with the C^{+} center (Table 5).

The internal potential energy diagram for rotation of the two aryl rings in the parent carbocation $\mathbf{3C}^{+}$ (H) is

Table 5. Geometric parameters and relative stabilities for **3C**$^+$ (H), **3C**$^+$(*p*-MeO), **3C**$^+$(*m*-Cl), **4C**$^+$(*p*-MeO), **4C**$^+$(*p*-Me) and **4C**$^+$(*m*-Cl) optimized at the RHF/6–31G* level[a]

Cations	Torsion angle (°)		Relative energy (kcal mol^{-1})	Bond length (Å)	
	θ_Y[b]	θ_X[c]		C^+—C_Y[b]	C^+—C_X[c]
4C$^+$ (X =Y = *p*-MeO)	$\underline{16.5}$	$\underline{40.1}$		$\underline{1.401}$	$\underline{1.431}$
4C$^+$ (X = Y = *p*-Me)	$\underline{18.2}$	$\underline{40.3}$		$\underline{1.409}$	$\underline{1.432}$
4C$^+$ (X = Y = *m*-Cl)	$\underline{18.9}$	$\underline{41.3}$		$\underline{1.415}$	$\underline{1.436}$
3C$^+$ (X = Y = H)	$\underline{18.8}$	$\underline{41.0}$	$\underline{0.0}$	$\underline{1.413}$	$\underline{1.435}$
(MP2/6–31G*)	($\underline{22.9}$)	($\underline{37.7}$)		($\underline{1.421}$)	($\underline{1.423}$)
	30	30	1.2		
	30	35.9[d]	0.9		
	0	53[e]	2.7		
3C$^+$ (X = *p*-MeO, Y = H)	$\underline{53.0}$	$\underline{8.1}$	$\underline{0.0}$	$\underline{1.470}$	$\underline{1.371}$
(MP2/6–31G*)	($\underline{44.7}$)	($\underline{14.9}$)		($\underline{1.439}$)	($\underline{1.402}$)
	60	0	0.9		
	45	0	2.4		
	30	0	8.4		
	30	30	4.2		
	0	45	9.1		
3C$^+$ (X = *m*-Cl, Y = H)	$\underline{15.5}$	$\underline{44.9}$	$\underline{0.0}$	$\underline{1.402}$	$\underline{1.447}$
(MP2/6–31G*)	($\underline{21.9}$)	($\underline{39.0}$)		($\underline{1.418}$)	($\underline{1.426}$)
	30	30	1.8		
	44.9	15.5	1.8		
9C$^+$ (X = *m*-Cl, Y = *p*-Me)	$\underline{11.4}$	$\underline{49.3}$		$\underline{1.386}$	$\underline{1.461}$

[a] Underlined data indicate those of the optimized structure.
[b] Between Y–phenyl and **C**$^+$.
[c] Between X–phenyl and **C**$^+$
[d] θ_2 for energy minimum with one phenyl fixed at $\theta_1 = 30°$.
[e] θ_2 for energy minimum with one phenyl fixed at $\theta_1 = 0°$.

shown in Fig. 7, where stabilization energies of the rotational conformer of the ion **3C**$^+$ (H) are plotted against the dihedral angles θ of coplanarity. When constraining a phenyl group to be coplanar ($\theta_1 = 0°$), a high potential energy is required for the second phenyl to be coplanar ($\theta_2 = 0°$), and the energy is lowered with increase in twisting from coplanarity to give a potential minimum at $\theta_2 = 53°$; however, this minimum potential energy for the conformation where one phenyl is coplanar and the other is twisted is significantly higher (2.7 kcal mol^{-1}) than the potential minimum of the most stable propeller conformer.

The angular profile of the potential energy diagram (Fig. 8) for the carbocation **3C**$^+$ (*p*-MeO), when constraining the *p*-methoxyphenyl ring to be coplanar (at $\theta_{p-\mathrm{MeO}} \approx 0°$), appears different from those of symmetrical **4C**$^+$ (*p*-MeO) and **3C**$^+$ (H). This conformation is 4.2 kcal mol^{-1} more stable than the doubly twisted propeller conformation ($\theta_{p-\mathrm{MeO}} \approx \theta_H \approx 30°$) and 9 kcal mol^{-1} more stable than the conformer with the phenyl-ring coplanar and *p*-methoxyphenyl twisted ($\theta_H = 0°$ and $\theta_{p-\mathrm{MeO}} > 45°$).

The geometry of the carbocation **BC**$^+$ should reflect the balance in resonance stabilizations by the two aryl groups, and the angles of rotation of the two aryl rings from coplanarity must depend upon the relative capabilities of X–and Y–aryl substituents for cation stabilization mainly by resonance. In symmetrically disubstituted cations **4C**$^+$ (X = Y), the two identical aryl rings are twisted equivalently out of the plane of the central C$^+$, denoted the ***E***-conformer, where both aryls are in a propeller-shaped conformation with $\theta_X = \theta_Y \approx 30°$. In unsymmetrically substituted cases (X ≠ Y), the stronger cation-stabilizing aryl ring should be less twisted from the same plane of the carbocation while the other ring should be twisted even more out of the plane. When the substituents X are more electron donating than Y, the cation **BC**$^+$ (X ≠ Y) takes a conformation (denoted the ***P***-conformer) where the variable X-phenyl is coplanar ($\theta_X \approx 0$); in this case, the substituent X in the coplanar aryl should then exert its maximum resonance effect on the solvolysis rate. On the other hand, when variable X substituents are less activating than the fixed Y–phenyl, the Y–phenyl retains coplanarity while constraining the X-substituted aryl ring to be more twisted; we denote this structure of X-aryl as the ***T***-conformation ($\theta_Y \approx 0$ and $\theta_X > 50°$) (cf. Scheme 1).

The symmetrical precursors **4** react through a transition state structurally close to the intermediate carbenium ion **4C**$^+$ with a preferred conformation of propeller shape. The *r* value of 1.19 found for the symmetrical set **4** must be the essential resonance demand of the diarylcarbocation **4C**$^+$ where X = Y or of the ***E***-conformer. The symmetry will be destroyed by replacing one phenyl by a ring substituted by an ED Y substituent, causing the Y-substituted phenyl ring to be more coplanar with the sp^2

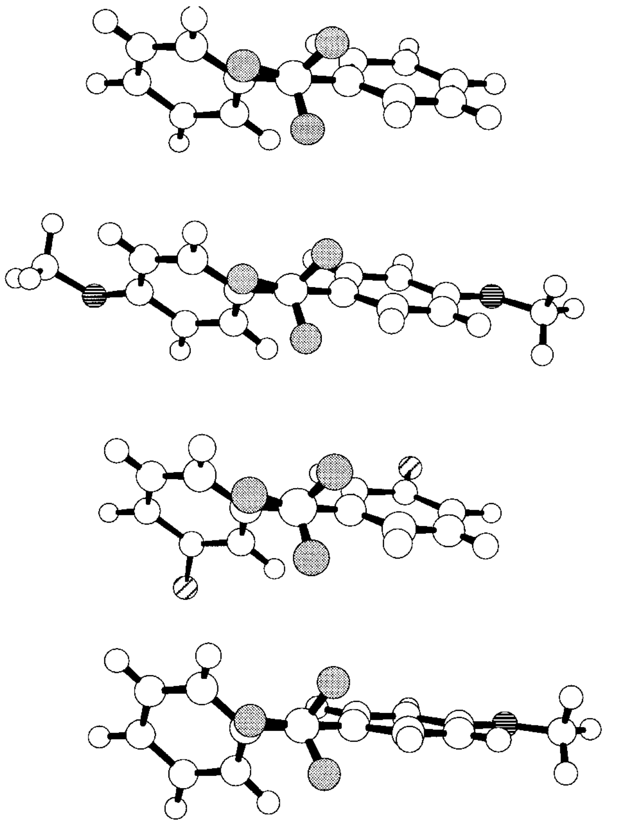


Figure 6. Optimized structures of α-CF_3-benzhydryl cations at the RHF/6–31G* level; from top to bottom, **3C**$^+$(H) with twist angles θ_{Ar-C^+} 18.8° on the right-hand and 41.0° on the left-hand; **4C**$^+$(*p*-MeO) with θ_{Ar-C^+} 16.5° and 40.1°; **4C**$^+$(*m*-Cl) with θ_{Ar-C^+} 18.9 and 41.3°; **3C**$^+$(*p*-MeO) with $\theta_{p\text{-}MeO}$ 8.1° and θ_H 53.0°.

cationic carbon. This will reduce the electronic demand on the X-substituted phenyl ring, which in turn will be forced to deviate further from coplanarity.

DISCUSSION

Structure–reactivity relationship in the α-CF_3-diarylcarbocation system

Despite the solvolysis of the symmetrically disubstituted series **4** where X = Y being correlated with Eqn. (1) with excellent precision (entry 4 in Table 3), the correlation results in Table 3 reveal that the Y–T equation is practically incapable of giving a single linear correlation for the whole range of X substituents in any fixed Y sets. The break in the Y–T correlation observed for a single set with X ≠ Y indicates the operation of different substituent interaction mechanisms for the different ranges of substituents involved, and can most likely be attributed to the substituent-induced change in conformation of the transition state.

Non-linear substituent effect correlations observed for

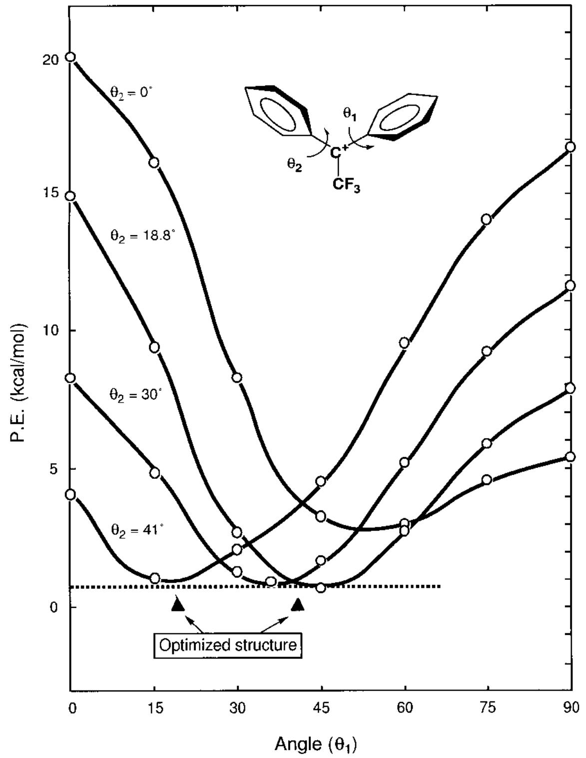


Figure 7. Angular profiles of potential energy of 1,1-diphenyl-2,2,2-trifluoroethyl cation **3C**$^+$(H) at the RHF/6–31 G* level

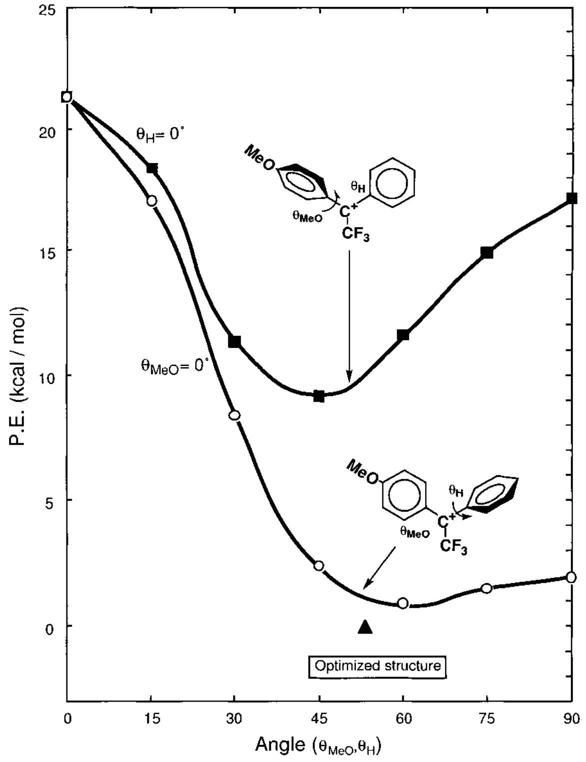


Figure 8. Angular profiles of potential energy of 1-(*p*-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl cation **3C**$^+$(*p*-MeO) at the RHF/6–31G* level

Y sets **7, 8** and **9** should be attributed to the occurrence of a changeover in conformation in the transition state within the range of X substituents studied. Not only for the symmetrical $\mathbf{4C}^+$ set but also for the substituent range in any sets where the X and Y are the same resonance class substituents, the preferred conformation should be essentially an equivalently twisted one (***E***-conformation). The range of s-ED class substituents in **7** (Y = *p*-PhO) satisfy a partial linear correlation [Eqn. (3)], whereas EW substituents show a significant deviation from the correlation in Eqn. (3), related to the non-equivalence of the effects of substituents X and Y (Fig. 1). The break in the Y–T correlation, in this case, appears to reflect the geometrical changeover from the ***E***- to the ***T***-conformation.

The substrates **7** carrying s-ED class X substituents should have a preferred conformation referred to as the geometry of the ***E***-conformation. The correlation for these substrates should be identical with that for **4**, which is characteristic of the equivalent diaryl-substituent effect associated with the ***E***-conformation. However, when the variable substituents X are distinctly weaker ED than the fixed Y substituent, the incipient carbocation $\mathbf{7C}^+$ or the transition state should have a ***T***-conformation in the set $\mathbf{7C}^+$; hence the partial correlation for the s-ED class X substituents may be related to the effect of X substituents in the ***E***-conformation, and that for the w-ED class substituents may be related to the effect of X–phenyl in the ***T***-conformer. The log k_H value (plotted as triangles in Fig. 1) for the unsubstituted member (X = H) in the correlation in Eqn. (3) of the ***E***-conformation in **7** should evidently be smaller than the log k_H value for the solvolysis of **7**, which is associated with the geometry of the ***T***-conformation.

Similarly, plots of log $(k/k_H)_\mathbf{8}$ values for s-ED class substituents of **8** with Y = *p*-MeO also fall on the correlation line with $\rho = -4.1$ [Eqn. (3)] for the ***E***-conformation, whereas w-ED class substrates show a correlation with a lower ρ for the ***T***-conformation, with a clear break of the Y–T correlation (Fig. 2).

The behavior of **9** where Y = *p*-Me appears to be appreciably different from that of **7** or **8**. Whereas the effects of w-ED class X groups ranging from *p*-Me to *p*-Cl can be described by Eqn. (3) for the ***E***-conformer correlation, both the s-ED and the EW classes X-groups deviate from the correlation line for the ***E***-conformation. Whereas the w-ED class substituents of $\mathbf{9C}^+$ have an ***E***-conformation, the s-ED class X-substituents have a ***P***-conformation, and the EW class X-substituents react via the ***T***-conformation. The Y–T correlation of this set **9** comprises three discrete linear relationships related respectively to ***P***-, ***E***- and ***T***-conformers, cf. entries 11–13 in Table 4. The correlation of the ***E***-conformer of $\mathbf{9C}^+$ coalesces into the correlation in Eqn. (2) for the $\mathbf{4C}^+$ series where X = Y or, more generally, Eqn. (3) for the equivalent diaryl substituent series. The plot (or log k_H) for the ***P***-conformer of the unsubstituted derivative **9** (X = H) appears to be lower than that for the corresponding ***E***-conformation.

In the monosubstituted set **3** where Y = H, both w-ED class substituents and *meta* substituents having equivalent $\bar{\sigma}_X$ values coalesce into the reference correlation for the ***E***-conformation [Eqn. (3)], whereas the s-ED class fall on a single correlation for the ***P***-conformation with a higher slope of $\rho = -6.1$. In set **5** where Y = *m*-Cl, s-ED class substituents show the characteristic $\rho = -6.2$ of the ***P***-conformation and the w-ED class show a slightly lower ρ value, and then the plot contacts the reference correlation [Eqn. (3)] at X = Y = *m*-Cl, at which the tangent ρ value must be identical with the ρ value for the ***E***-conformation.

For the set **6** where the X substituents involved are all more cation stabilizing than the fixed Y = 3,5-Cl_2 the s-ED and w-ED class substituents should all be in the ***P***-conformation, which gives a single linear Y–T correlation with a high ρ value of -6.0. This correlation (entry 6 in Table 4) should be characteristic of the ***P***-conformation where the Y–T correlation should represent the effect of entirely conjugating X–aryl substituents for the whole range involved.

For all the Y sets, the *r* value can be related to rotation from coplanarity with the incipient carbocation center, and given as a function of the dihedral angle θ between the X-substituted aryl ring and the plane of the carbocation,[5b,10,16,17] to follow an equation of the form

$$r_\theta / r_{\max} = \cos^2\theta \qquad (4)$$

where $r_{\max}$ is the resonance demand of the aryl group in the ***P***-conformation and r_θ is the *r* for the effect of X–aryl in the actual situation at dihedral angle θ of the X–phenyl ring plane. Hence, the *r* values for the respective conformers of any sets can be estimated from this conformation dependence. The $r_{\max}$ value for the ***P***-conformation of **7** and **8**, although not yet at hand, is expected to be 1.45, provided an r_θ value of 1.2 for the ***E***-conformer with $\theta \approx 25°$. The apparent resonance demand in any Y set is a function of preferred conformations, and therefore dependent on the range of substituents in the set. Accordingly, in order to discuss the intrinsic resonance demand of the system, we have to compare the effects of varying X-substituted phenyls kept in the same conformation for a series of Y sets. In consequence, the intrinsic resonance demand of the ***P***-conformers in this system varies even less significantly, within a range from 1.4 to 1.7, for a wide change of the Y substituent from *p*-methoxy to 3,5-Cl_2. This interpretation, of course, relies upon the validity of the carbocation model of the transition state, implying the closeness of the structure or the reaction coordinate between the transition state and the intermediate carbocation.

While the interpretation in terms of varying coplanarity applies fairly consistently to the variation of the *r* value observed in this system, another significant feature

Table 6. ρ and $(\log k_H)_Z$ values for solvolyses of α-trifluoromethylbenzyl tosylates in 80% aqueous ethanol at 25 °C

System $PhC(Z)CF_3$ or $PhC(PhY)CF_3$	k_t^H (s^{-1}) at 25 °C	$(\log k_H)_Z$	ρ
1, Z = Me	7.497×10^{-7}	−6.13	−6.29
2, Z = H	3.067×10^{-11a}	−10.51	−6.05
3, Y = H	2.677×10^{-3}	−2.57	−4.33 −6.08
4, Y = Y	2.677×10^{-3}		−4.15
5, Y = *m*-Cl	5.279×10^{-5}	−4.28	−4.81 −6.19
6, Y = 3,5-Cl_2	2.736×10^{-6}	−5.56	−5.95
8, Y = *p*-MeO	1.980×10^{3}	3.30	−3.94 −1.71
7, Y = *p*-PhO	2.235×10	1.35	−4.01 −2.04
9, Y = *p*-Me	8.046×10^{-2}	−1.09	−6.26 −3.66 −2.91

[a] Estimated value from the data in other solvents.[8]

that we observed clearly in this system is the significant dependence of ρ on both X and Y substituents. In all the Y sets of system **B**, the ρ value varies significantly with varying classes of X substituents within an individual Y set. This must also be ascribed to the varying coplanarity of aryl rings caused by the change of the two substituents.

The correlation results in Table 3, from the ordinary viewpoint, reveal that the ρ value assigned for the effects of variable X substituents varies significantly depending upon fixed Y substituents. While the substituent effect correlations are apparently non-linear or bilinear for most of the Y sets except only for a set with Y = 3,5-Cl_2, the apparent ρ values for these non-linear correlations change significantly depending on the change in Y substituents; either the higher ρ value or the lower value for the bilinear correlation also shows a significant variation with Y sets. There is an apparent tendency that the ρ value becomes more negative as Y becomes more EW. Closely similar dependences of ρ upon changing Y substituents are found even more significantly in the behavior of the ρ^+ in the corresponding Brown correlations (cf. Table 3).

The dependence of ρ_Y upon $\bar{\sigma}_Y$ for the second (fixed) aryl substituents Y in α, α-diarylcarbocation formation (series **B**) is referred to as the non-additivity relationship, which can be rewritten in the form[14]

$$\rho_Y = q\bar{\sigma}_Y + \rho_H \tag{5}$$

This equation has been discussed for the solvolyses of benzhydryl chlorides[18] and the bromination of α, α-diarylethylenes.[14,19] The varying ρ values in a related series of reactions can be related to the cationic charge developed at the reaction center in the transition state. Concerning the series **A**, there is also more general behavior of ρ value referred to as the quantitative reactivity–selectivity relationship,[13] that is, an inverse-linear relationship of the selectivity ρ_Z against the reactivities $(\log k_H)_Z$ of members of respective Z sets:

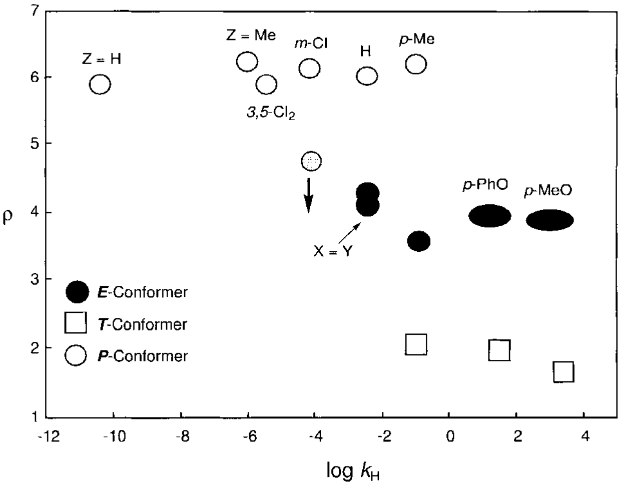


Figure 9. Reactivity–selectivity relationship; ρ_Z or ρ_Y values vs $\log (k_H)_Z$ or $\log (k_H)_Y$ for α-CF_3-benzyl systems (**A** and **B**)

$$\rho_Z = S(\log k_H)_Z + \text{constant} \tag{6}$$

Either the *q* coefficient in Eqn. (5) or the *S* coefficient in Eqn. (6) can be intimately related to the α exponent in the extended Brønsted equation and therefore can be a measure of the early–late shift of the transition state coordinate in the reaction series.[15]

Equation (6) can be most conveniently used for this system, as we have extended here the discussion concerning the behavior of selectivity not only for the α-CF_3_α, α-diarylmethyl system (**B**) but also for the α-Z-α-CF_3-benzyl system (**A**) liberating $XC_6H_4C^+(Z)CF_3$ (**AC**$^+$). Indeed, as in Table 6, the reactivity $(\log k_H)_Z$ changes over a range of 7.9 log units from −10.5 for **A** (Z = H), −6.1 for **A** (Z = CH_3) to −2.57 for **A** (Z = C_6H_5). By including **7, 8** and **9** in the series **B** as members of **A** with Z = *p*-MeC_6H_4–*p*-$MeOC_6H_4$, the $(\log k_H)_Z$ scale for the series **A** can be extended towards higher reactivity by over 13.8 log units. The reactivity–selectivity relationship in Eqn. (6) for the present system is illustrated in Fig. 9. It is most remarkable that the ρ value remains within good constancy of −6.14 ± 0.11 for a change in reactivity of 9 log units, whereas for the diaryl series, **3, 5** and **9**, this high ρ value is observed only for the ED range of substituents. Note again that the apparent ρ for the s-ED class substituent range in any Y sets should be unambiguously estimated to give exact values regardless of the *r* value (see above).

On the other hand, the sets with Z = *p*-$PhOC_6H_4$ and *p*-$MeOC_6H_4$ at the higher reactivity scale in series **A** give for the range of s-ED class substituents a distinctly low ρ value of −4.0, a value which is obviously different from

Table 7. Physical and analytical data for 1,1-diary1-2,2,2-trifluoroethyl alcohols, chlorides and bromides

Substituent			Carbon (%)		Hydrogen (%)	
X	Y	M.p. (°C)	Found	Calculated	Found	Calculated
Alcohols						
p-PhO	*p*-MeO-*m*-Cl	Liq.	61.60	61.70	3.97	3.94
p-PhO	3,4-Me_2	124–126	70.99	70.96	5.21	5.14
p-PhO	*p*-MeS-*m*-Cl	Liq.	59.43	59.37	3.88	3.80
p-PhO	*p*-F	Liq.	66.40	66.30	3.95	3.89
p-PhO	*p*-MeS	Liq.	64.72	64.61	4.51	4.39
p-MeO	*p*-MeS	Liq.	58.54	58.53	4.83	4.60
p-MeO	*p*-F	Liq.	60.20	60.00	4.25	4.03
p-MeO	*p*-MeS-*m*-Cl	Liq.	53.12	52.97	3.97	3.89
p-Me	3,5-Me_2	Liq.	69.35	69.38	5.91	5.82
p-Me	*p*-Cl	Liq.	59.72	59.91	4.29	4.02
p-Me	*p*-*t*-Bu	75–77	70.67	70.79	6.56	6.57
p-Me	*p*-MeO-*m*-Cl	Liq.	58.31	58.11	4.38	4.27
p-Me	*p*-MeS	Liq.	61.71	61.53	4.95	4.84
p-Me	*p*-MeS-*m*-Cl	Liq.	55.61	55.41	4.26	4.07
Chlorides						
p-MeO-*m*-Cl	3,5-Cl_2	91–92	44.70	44.59	2.30	2.25
p-PhO	*p*-MeO-*m*-Cl	78–79	59.14	59.04	3.66	3.54
p-MeO	*p*-MeO-*m*-Cl	65–68	52.66	52.63	3.69	3.59
Bromides						
p-Me	*p*-*t*-Bu	61–62.5				
p-Me	3,5-Me_2	44–46				

the ρ value of -6.1 expected from extrapolation to $S = 0$ in the reactivity–selectivity correlation for the series **A**. It is worthy of note that there is an excellent linear Y–T correlation for **4** with a ρ value of -4.1 encompassing the entire range of substituents of over 11 log units of reactivity from bis-(*p*-methoxyphenyl) to bis-(*m*-chlorophenyl).[10]

The ρ value should also be related to the conformation of the incipient carbocation, i.e. to the angular deviation of the variable X-substituted aryl ring from coplanarity in the carbocation. The s-ED class X-substituents in **3, 5, 6** and **9** gave a constant ρ value of -6.1, a value which can be referred to as the effect of X in the coplanar aryl ring in the ***P***-conformer. On the other hand, the EW class X substituents in these Y sets are found to give a constant ρ value of -4.1, which is referred to as the ρ value reflecting the effect of X–phenyl in the ***E***-conformer. The same ρ value was obtained for the symmetrical **4** in the ***E***-conformation.

The failure in linearly correlating the whole-substituent effect in any fixed Y set in the series **B** is certainly due to the complexity associated with the conformational change in the propeller-shaped, twisted carbocationic structure of the transition state. The observed variation of the ρ value just demonstrates the dependence of the selectivity ρ upon the deviation from the propeller conformation of diaryl carbocations. Most important, the ρ values for the same conformers are essentially constant for the respective conformations, independent of varying Y substituents, but more data would be required. Despite the significant change in ρ value, there must be little or no change in the apparent position of the transition state.

Dubois *et al.*[19] pointed out in the bromination of 1,1-diarylethylenes that the ρ value increased significantly as the fixed Y became more EW, and the range of substituents X on which the ρ for respective Y sets were based evidently differed from set to set. The RHF/6–31 G* optimization of the corresponding α, α-diphenylethyl cations suggests structures of propeller geometry, with a comparable twisting angle of ca 30° to that in the cation **4C**$^+$.[20] Accordingly, bromination should show a similar conformational dependence of substituent effects to the above. While significant variations of apparent ρ values observed in solvolyses of the related polyaryl carbocation systems have frequently been ascribed to the shift of the transition state coordinate, those conclusions for the coordinate shift should be reconsidered precisely from the point of the above conformation dependence.

EXPERIMENTAL

Materials. α, α, α-Trifluoroacetophenones required for preparation of alcohol precursors of solvolysis substrates were synthesized according to Stewart's procedure for the Grignard reaction of substituted bromobenzenes with trifluoroacetic anhydride at -78 °C in a dry ice–acetone bath.[8a,21]

Trifluoroacetophenones were converted into the corresponding 1,1-diaryl-2,2,2-trifluoroethanols by the Grignard reaction with substituted phenylmagnesium bromide at ice-bath temperature.[1,10] The tertiary alcohols obtained were purified by column chromatography on silica gel.

1,1-Diaryl-2,2,2-trifluoroethyl bromides were prepared from the alcohol and phosphorus tribromide by essentially the same procedure as reported by Liu and coworkers[10–12,22] The bromide was purified through column chromatography on alumina. Some of bromides were not easily purified and were utilized directly for kinetic measurements. The chlorides were prepared from the chlorination of alcohols with $SOCl_2$ and dry pyridine.[10–12]

Physical constants and analytical data are listed in Table 7.

Solvents.[1,10] Commercial 95% ethanol was dehydrated twice by heating under reflux with magnesium ethoxide and distilled. Deionized water was refluxed with $KMnO_4$ and the distillate was redistilled immediately before use. Aqueous (80%) ethanol (80E) was prepared by mixing corresponding volumes of ethanol (80 parts) and water (20 parts) at 25 °C.

Kinetic measurement. Solvolysis rates were measured by a conductimetric method as described before.[1,10] The first-order rate constants were determined by a least-squares computer program; the precision of fit to first-order kinetics was generally satisfactory over 2.5 half-lives with correlation coefficient >0.99998. The experimental errors in the respective runs were generally less than 1.0% and the reproducibility of the rate constants was within ±1.5%.

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