

THE SPIN DELOCALIZATION SUBSTITUENT PARAMETER  $\sigma_{JJ}$ .  
 5. CORRELATION ANALYSIS OF  $^{19}\text{F}$  CHEMICAL SHIFTS OF  
 SUBSTITUTED TRIFLUOROSTYRENES.  
 THE UNRESOLVED POLAR SUBSTITUENT PARAMETER  $\sigma_{mb}$

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The  $^{19}\text{F}$  NMR spectra of 30 substituted  $\alpha,\beta,\beta$ -trifluorostyrenes (Y-TFSs, 1) covering a diverse range of substituents are reported and discussed. Values ( $\delta_{\text{F}^1}$ ,  $\delta_{\text{F}^2}$ ,  $\Delta\delta_{3-1}$  and  $\Delta\delta_{3-2}$ ) derived from the  $^{19}\text{F}$  NMR chemical shifts of the fluorine atoms of 1 are found to correlate very well with  $\sigma_1$  and  $\sigma_{\text{R}}^0$ . The results of the correlations of the  $^{19}\text{F}$  chemical shifts with dual ( $\sigma_{\text{F}}$  and  $\sigma_{\text{R}}$ ) and triple parameter ( $\sigma_{\text{F}}$ ,  $\sigma_{\text{R}}$  and  $\sigma_{\text{a}}$ ) treatments are compared. An unresolved substituent parameter  $\sigma_{mb}$ , is proposed for applications to systems in which the substituent Y interacts with a multiple bond and is compared with  $\sigma^+$ .

INTRODUCTION

Over the past decade, efforts toward the establishment of a spin delocalization substituent parameter  $\sigma^{\cdot}$  have intensified.<sup>1-7</sup> One approach is the treatment of kinetic data of the radical reactions in terms of the extended Hammett equation:<sup>5,8</sup>

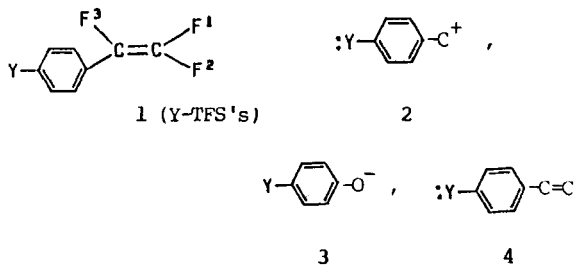
$$\log(k/k_{\text{H}}) = \rho^{\cdot}\sigma^{\cdot} + \rho^{\cdot}\sigma^{\cdot} \quad (1)$$

where  $\sigma^{\cdot}$  is an unresolved polar substituent parameter that reflects the total contribution of all polar effects<sup>9</sup> to that particular radical reaction. Ideally, each particular radical reaction used for the establishment of a certain  $\sigma^{\cdot}$  scale should have its own best suited  $\sigma^{\cdot}$

scale.<sup>8,10,11</sup> With the final objective of setting up a truly reliable  $\sigma^{\cdot}$  scale, to be designated  $\sigma_{JJ}$ , this work represents efforts to establish an independently measured  $\sigma^{\cdot}$  scale specifically suited to our  $\sigma^{\cdot}$  approach with the cyclodimerization of substituted trifluorostyrenes (Y-TFSs, 1) as the radical reaction.<sup>12,13</sup>

Hammett-type substituent parameters, such as  $\sigma_{\text{p}}$ ,  $\sigma_{\text{m}}$ ,  $\sigma^+$  and  $\sigma^-$ , are examples of unresolved polar substituent parameters, and they have been established as very useful and of wide applicability. In order to understand the nature of these parameters, Taft and co-workers<sup>8,11</sup> have resolved them into several contributing components of factors, namely, field, resonance, polarizability and electronegativity effects. They are resolved polar substituent parameters and are designated as  $\sigma_{\text{F}}$ ,  $\sigma_{\text{R}}$ ,  $\sigma_{\text{a}}$  and  $\sigma_{\text{x}}$  respectively. Both classes of substituent parameters (unresolved and resolved) are valuable assets in basic organic chemistry.

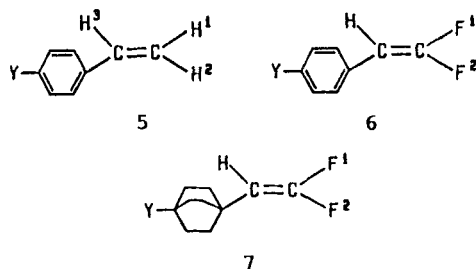
One of the most popular  $\sigma^{\cdot}$  parameter is  $\sigma^+$ ; it is best suited for systems in which the substituent Y interacts with an electron-deficient centre, e.g. an empty orbital, as in 2.<sup>14</sup> On the other hand,  $\sigma^-$  is derived from systems in which Y interacts with a negative centre, as in 3.<sup>15</sup> Our Y-TFS system represents yet another type of system in which Y interacts with a multiple bond, as in 4, thus the  $\sigma^{\cdot}$  derived therefrom might be designated as ' $\sigma_{mb}$ ', if proved to be useful and applicable to other



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studies in the future. One noteworthy and distinct difference between the systems designed for  $\sigma^+$  (2) and  $\sigma_{mb}$  (4) is that in the latter, there exists a repulsive term between the double bond and the lone pair (n-) electrons on Y or  $\pi$ -electrons in Y (e.g. Y = vinyl).<sup>16,17</sup> This repulsive term is magnified by the lone pairs on the fluorine atoms of Y-TFS (1).<sup>17</sup>

Fluorine-19 and carbon-13 NMR have been widely and successfully applied to studies of polar substituent parameters.<sup>10,18</sup> Craik and Brownlee<sup>10</sup> have reviewed the substituent effects on the side chain chemical shifts in the ring substituted styrene derivatives, and mentioned that this system is a very useful probe for studying the substituent effects of Y on the structural and electronic properties of this framework. Reynolds and co-workers and Adcock and Kok have successfully applied the correlation analysis of substituent effects with <sup>19</sup>F and <sup>13</sup>C NMR in substituted styrenes (5),<sup>19</sup>  $\beta,\beta$ -difluorostyrenes (6)<sup>20</sup> and 1,1-difluoro-2-(4-substituted-bicyclo[2,2,2]oct-1-yl)ethenes (7).<sup>21</sup>



In this work, the <sup>19</sup>F chemical shifts of 30 Y-TFSs have been correlated with field/inductive and resonance effects, and an unresolved substituent parameter  $\sigma_{mb}$  is proposed for applications to systems in which the substituent interacts with the multiple bond.

## EXPERIMENTAL

The Y-TFSs were synthesized by methods reported previously.<sup>12,17,22</sup> <sup>19</sup>F NMR spectral data were obtained on Varian XL-200 (188.2 MHz) and Varian EM-360 L (56.4 MHz) spectrometers operating at a probe temperature of 20 °C. Spectra were measured for 0.2 M solutions in hexane. The measurements were repeated at least five times on the EM-360 or twice on the XL-200. On the basis of these measurements, a conservative estimate of the uncertainty in the <sup>19</sup>F chemical shifts is 0.1 ppm and in the <sup>19</sup>F-<sup>19</sup>F coupling constants 2 Hz.

## RESULTS AND DISCUSSION

### <sup>19</sup>F NMR of Y-TFS

The <sup>19</sup>F NMR data for Y-TFSs in hexane as the solvent

are given in Table 1. These shifts were determined and assigned from an analysis of the AMX <sup>19</sup>F NMR spectra. As pointed out previously,<sup>13,23</sup> the chemical shifts of F<sup>1</sup> and F<sup>2</sup>, as well as the differences of the chemical shifts of F<sup>3</sup> and F<sup>1</sup>, or F<sup>3</sup> and F<sup>2</sup>, i.e.  $\delta_{3-1} = \delta_{F^3} - \delta_{F^1}$ , or  $\delta_{3-2} = \delta_{F^3} - \delta_{F^2}$ , reflect the degree of polarization of the double bond in Y-TFS.<sup>17</sup> In this work, the unsubstituted TFS is taken as the standard, and the differences in chemical shifts are defined by the equations

$$\Delta\delta_{3-1} = (\delta_{3-1})_Y - (\delta_{3-1})_H \quad (2)$$

$$\Delta\delta_{3-2} = (\delta_{3-2})_Y - (\delta_{3-2})_H \quad (3)$$

On the basis of the  $\Delta\delta_{3-1}$  and  $\Delta\delta_{3-2}$  values, the degree of polarization of the  $\pi$ -bond in Y-TFS decreases in the following order for *para* substituents:

CN, NO<sub>2</sub> > COCH<sub>3</sub> > CF<sub>3</sub> > COOCH<sub>3</sub> > Me<sub>3</sub>Si,

Br > Cl > Ph, Vinyl > H > CH<sub>3</sub>S > *t*-Bu >

F > CH<sub>3</sub> > *c*-Pr > PhO > OH > CH<sub>3</sub>O > NMe<sub>2</sub>

and for *meta* substituents:

CF<sub>3</sub> > Br > F > Cl > H > CH<sub>3</sub>O > Et > *t*-Bu > CH<sub>3</sub>

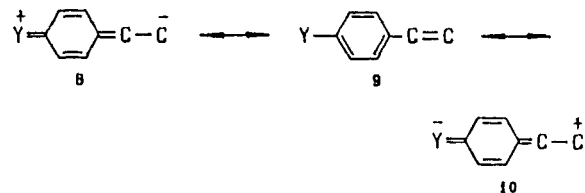
### Correlation analysis of <sup>19</sup>F chemical shifts of Y-TFS

Based on the NMR investigations of a series of substituted styrene derivatives, Reynolds *et al.*<sup>24</sup> concluded that (i) a dual substituent parameter treatment ( $\sigma_F$  and  $\sigma_R^0$ ) is necessary to account adequately for substituent-induced long-range chemical shifts in styrenes and (ii) the actual substituent chemical shifts (SCS) reflect a combination of resonance and field/inductive (polarization) effects. This work makes use of both Exner's extensive compilation<sup>25</sup> and recent work by Taft and Topsom<sup>8</sup> and analyses our data with  $\sigma_I$ ,  $\sigma_R^0$ ,  $\sigma_\alpha$ ,  $\sigma_F$  and  $\sigma_R$  parameters. The equation

$$\text{Variable} = \rho_I\sigma_I + \rho_R\sigma_R^0 \quad (4)$$

is used for the correlation of our data with Exner's  $\sigma_I$  and  $\sigma_R^0$  values, where 'variable' represents the SCS values or differences in SCS values of the ten *para*- and *meta*-substituted probes, namely *p*- $\delta_{F^1}$ , ..., *p*- $\Delta\delta_{3-1}$ , ..., *m*- $\Delta\delta_{3-2}$ , etc., as given in Table 2.

Table 2 shows that the data for  $\delta_{F^1}$ ,  $\delta_{F^2}$ ,  $\Delta\delta_{3-1}$  and  $\Delta\delta_{3-2}$  correlate very well with  $\sigma_I$  and  $\sigma_R^0$ , but  $\delta_{F^3}$  does not. As shown in Scheme 1, the contributions of the



Scheme 1

Table 1.  $^{19}\text{F}$  NMR data for Y-TFS (0.2 M in hexane)

No.	Y	$^{19}\text{F}$ chemical shifts <sup>a</sup>					Coupling constants (Hz)		
		$\delta_{\text{F}^1}$	$\delta_{\text{F}^2}$	$\delta_{\text{F}^3}$	$\Delta\delta_{3-1}$	$\Delta\delta_{3-2}$	$J_{12}$	$J_{13}$	$J_{23}$
1	H	23.96	38.46	100.12	0	0	73	33	109
2	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	29.35	44.36	100.05	-5.46	-5.97	84	32	110
3	<i>p</i> -OCH <sub>3</sub>	26.55	41.63	98.45	-4.26	-4.84	82	38	118
4	<i>p</i> -OH	26.98	42.22	99.42	-3.71	-4.40	79	34	111
5	<i>p</i> -OPh	24.50	39.60	98.34	-2.32	-2.92	77	33	113
6	<i>p-c</i> -C <sub>3</sub> H <sub>7</sub>	24.83	39.17	99.61	-1.38	-1.22	75	31	109
7	<i>p</i> -CH <sub>3</sub>	25.18	39.74	100.08	-1.25	-1.32	81	37	114
8	<i>p</i> -F	24.42	39.70	99.65	-0.93	-1.80	80	32	115
9	<i>p-t</i> -C <sub>4</sub> H <sub>9</sub>	24.11	38.82	99.45	-0.82	-1.03	74	32	111
10	<i>p</i> -SCH <sub>3</sub>	24.93	39.77	100.51	-0.58	-0.92	75	34	108
11	<i>p</i> -CH=CH <sub>2</sub>	23.86	38.53	100.80	0.78	0.61	71	33	109
12	<i>p</i> -C <sub>6</sub> H <sub>5</sub>	23.66	38.56	100.62	0.80	0.40	71	33	109
13	<i>p</i> -CONH <sub>2</sub> <sup>b</sup>	23.88	38.03	101.23	1.19	1.50	73	36	113
14	<i>p</i> -Cl	22.30	37.50	99.70	1.24	0.74	75	35	115
15	<i>p</i> -Br	23.27	38.20	100.80	1.37	0.94	72	38	113
16	<i>p</i> -Si(CH <sub>3</sub> ) <sub>3</sub>	22.70	37.28	100.31	1.45	1.37	71	33	109
17	<i>p</i> -COOH <sup>b</sup>	23.14	37.16	101.77	2.47	2.94	66	36	111
18	<i>p</i> -COOCH <sub>3</sub>	22.51	37.18	102.25	3.09	3.41	66	36	107
19	<i>p</i> -CF <sub>3</sub>	21.04	36.08	100.81	3.61	3.05	66	38	113
20	<i>p</i> -COCH <sub>3</sub>	21.02	35.77	101.24	4.06	3.81	64	34	109
21	<i>p</i> -NO <sub>2</sub>	19.89	34.86	102.00	5.95	5.48	58	38	111
22	<i>p</i> -CN	20.81	35.66	102.93	5.96	5.62	62	38	111
23	<i>m</i> -CH <sub>3</sub>	23.87	38.34	99.33	-0.70	-0.67	80	37	112
24	<i>m-t</i> -C <sub>4</sub> H <sub>9</sub>	23.40	38.40	98.90	-0.66	-1.16	75	36	113
25	<i>m</i> -C <sub>2</sub> H <sub>5</sub>	24.41	39.14	100.19	-0.38	-0.61	75	32	109
26	<i>m</i> -OCH <sub>3</sub>	24.04	38.37	100.07	-0.13	0.04	79	34	109
27	<i>m</i> -Cl	21.60	35.20	99.10	1.34	2.24	68	34	109
28	<i>m</i> -F	22.72	36.80	100.90	2.02	2.44	71	32	107
29	<i>m</i> -Br	21.97	36.89	100.96	2.83	2.41	68	34	110
30	<i>m</i> -CF <sub>3</sub>	21.77	36.42	100.93	3.00	2.85	69	34	110

<sup>a</sup> In ppm relative to external CF<sub>3</sub>COOH; high-field shifts are positive.<sup>b</sup> Measured in 0.2 M THF solution.Table 2. Values of  $\rho_{\text{I}}$  and  $\rho_{\text{R}}$  of equation (4) and corresponding values of the correlation coefficient  $R$ , standard deviation  $s$ ,  $F$ -test<sup>a</sup> and  $\psi$ <sup>b</sup> for correlation of  $^{19}\text{F}$  NMR of ten probes as variables of equation (4) with substituent parameters  $\sigma_{\text{I}}^{\text{c}}$  and  $\sigma_{\text{R}}^{\text{0c}}$ 

Variable	$\rho_{\text{I}}$	$\rho_{\text{R}}$	$R$	$s$	$F^{\text{d}}$	$\psi$	$n^{\text{e}}$
<i>p</i> - $\delta_{\text{F}^1}$	$-3.37 \pm 0.87$	$-8.87 \pm 0.83$	0.962	0.66	104	0.27	20
<i>p</i> - $\delta_{\text{F}^2}$	$-2.76 \pm 0.87$	$-9.45 \pm 0.83$	0.963	0.66	108	0.29	20
<i>p</i> - $\delta_{\text{F}^3}$	$0.76 \pm 0.90$	$4.10 \pm 0.86$	0.816	0.71	17	0.63	20
<i>p</i> - $\Delta\delta_{3-1}$	$4.54 \pm 0.76$	$12.81 \pm 0.72$	0.988	0.50	361	0.16	20
<i>p</i> - $\Delta\delta_{3-2}$	$3.54 \pm 0.75$	$13.55 \pm 0.71$	0.990	0.49	401	0.15	20
<i>m</i> - $\delta_{\text{F}^1}$	$-4.05 \pm 1.03$	$-2.94 \pm 1.61$	0.924	0.48	17	0.47	9
<i>m</i> - $\delta_{\text{F}^2}$	$-4.73 \pm 1.21$	$-2.18 \pm 1.62$	0.891	0.67	12	0.56	9
<i>m</i> - $\delta_{\text{F}^3}$	$1.79 \pm 1.29$	$1.14 \pm 2.02$	0.554	0.77	1	1.02	9
<i>m</i> - $\Delta\delta_{3-1}$	$5.82 \pm 1.02$	$4.00 \pm 1.59$	0.962	0.47	37	0.34	9
<i>m</i> - $\Delta\delta_{3-2}$	$6.53 \pm 0.86$	$3.32 \pm 1.35$	0.983	0.34	86	0.23	9

<sup>a</sup> Ref. 26.<sup>b</sup> Refs 27 and 28b.<sup>c</sup> Ref. 21.<sup>d</sup> Critical  $F$  values:  $F_{0.001(2,17)} = 10.66$ ,  $F_{0.001(2,6)} = 27.00$ .<sup>e</sup> Number of data.

resonance effect to the ground state of the conjugated molecules can be represented by various symbolic resonance forms (8 or 10). They might help us to visualize an important difference between the  $\alpha$ -C and  $\beta$ -C of the side-chain in that the  $\beta$ -C is at the terminus of the resonance system whereas the  $\alpha$ -C is not, and therefore the electron density changes at the  $\beta$ -C may be more directly affected by the *para* substituents. Consequently, the chemical shifts of F<sup>1</sup> and F<sup>2</sup> correlate with  $\sigma_1$  and  $\sigma_R^0$  much better than does F<sup>3</sup>.

The relative importance of resonance and field/inductive effects may be assessed by application of the equation<sup>28</sup>

Resonance (%)

$$= \frac{100\rho_R [\Sigma(\sigma_R^0 - \bar{\sigma}_R^0)^2]^{1/2}}{\rho_R [\Sigma(\sigma_R^0 - \bar{\sigma}_R^0)^2]^{1/2} + \rho_I [\Sigma(\sigma_1 - \bar{\sigma}_1)^2]^{1/2}} \quad (5)$$

Table 3. Relative importance of the resonance (*R*) effects as expressed by equation (5) and estimated by different variables

Variable	<i>R</i> (%)	Variable	<i>R</i> (%)
<i>p</i> - $\delta_{F^1}$	76.4	<i>m</i> - $\delta_{F^1}$	47.2
<i>p</i> - $\delta_{F^2}$	80.8	<i>m</i> - $\delta_{F^2}$	46.6
<i>p</i> - $\delta_{F^3}$	86.9	<i>m</i> - $\delta_{F^3}$	43.9
<i>p</i> - $\Delta\delta_{3-1}$	77.6	<i>m</i> - $\Delta\delta_{3-1}$	45.8
<i>p</i> - $\Delta\delta_{3-2}$	82.5	<i>m</i> - $\Delta\delta_{3-2}$	38.5

Table 4. Values of  $\rho_F$ ,  $\rho_R$  and  $\rho_\alpha$  of equation (6) and corresponding values of the correlation coefficient *R*, standard deviation *s* and  $\psi$  for correlations of <sup>19</sup>F chemical shifts of 15 Y-TFSs with substituent parameters  $\sigma_F^a$ ,  $\sigma_R^a$  and  $\sigma_\alpha^a$

Variable	$\rho_F$	$\rho_R$	$\rho_\alpha$	<i>R</i>	<i>s</i>	$\psi$
<i>p</i> - $\delta_{F^1}$	-4.19 ± 1.12	-8.91 ± 0.95	0.61 ± 0.78	0.972	0.69	0.27
<i>p</i> - $\Delta_{F^2}$	-3.36 ± 1.09	-9.58 ± 0.93	0.75 ± 0.80	0.976	0.66	0.25
<i>p</i> - $\delta_{F^3}$	2.32 ± 1.37	1.50 ± 1.16	-0.32 ± 0.95	0.595	1.04	0.94
<i>p</i> - $\Delta\delta_{3-1}$	6.55 ± 1.14	11.57 ± 0.96	-1.63 ± 0.79	0.984	0.71	0.21
<i>p</i> - $\Delta\delta_{3-2}$	5.76 ± 1.16	12.38 ± 0.98	-1.19 ± 0.81	0.984	0.74	0.21

<sup>a</sup> Ref. 8.

Table 5. Values of  $\rho_F$  and  $\rho_R$  of equation (7) and corresponding values of the correlation coefficient *R*, standard deviation *s* and  $\psi$  for correlations of <sup>19</sup>F NMR of 15 Y-TFSs with substituent parameters  $\sigma_F^a$  and  $\sigma_R^a$

Variable	$\rho_F$	$\rho_R$	<i>R</i>	<i>s</i>	$\psi$
<i>p</i> - $\Delta_{F^1}$	-3.86 ± 1.04	-9.06 ± 0.93	0.970	0.69	0.27
<i>p</i> - $\delta_{F^2}$	-2.95 ± 1.02	-9.76 ± 0.92	0.973	0.67	0.26
<i>p</i> - $\delta_{F^3}$	1.75 ± 1.14	3.08 ± 1.02	0.768	0.82	0.72
<i>p</i> - $\Delta\delta_{3-1}$	5.67 ± 1.15	11.97 ± 1.03	0.975	0.85	0.25
<i>p</i> - $\Delta\delta_{3-2}$	6.55 ± 1.19	11.47 ± 1.12	0.972	0.91	0.26

<sup>a</sup> Ref. 8.

and the resonance values thus obtained are summarized in Table 3. The results are in accord with expectations.

Since the styrene derivatives are highly polarizable systems, the substituent polarizability effect might affect the chemical shifts of Y-TFSs.<sup>29,30</sup> Tables 4 and 5 show the results of the triple parameter correlation analysis of <sup>19</sup>F data with  $\sigma_F$ ,  $\sigma_R$  and  $\sigma_\alpha$  by equation (6), and the corresponding dual parameter correlation without  $\sigma_\alpha$  by equation (7).

$$\text{Variable} = \rho_F\sigma_F + \rho_R\sigma_R + \rho_\alpha\sigma_\alpha + C \quad (6)$$

$$\text{Variable} = \rho_F\sigma_F + \rho_R\sigma_R + C \quad (7)$$

Qualitative comparison of the standard deviations (*s*) and  $\psi$  values indicates that the triple parameter correlation is slightly better than the dual parameter correlation. Taking  $\Delta\delta_{3-1}$  as an example, the *s* value is 0.71 (*s*<sub>1</sub>) for the former and 0.85 (*s*<sub>2</sub>) for the latter. Based on the variance test of the correlation,<sup>26</sup> the variance ratio *F'* of the dual parameter correlation to the triple parameter correlation  $s_2^2/s_1^2$  is equal to 1.43. At the significance level  $\alpha = 0.05$ , the critical *F'* value  $F_{0.05(12,13)}$  is 2.60,<sup>26</sup> which is larger than 1.43. This indicates that there is no significant difference between the standard deviations of the dual and triple regressions at the significance level  $\alpha = 0.05$ . Factor analysis also shows that the correlation analysis of <sup>19</sup>F chemical shifts of Y-TFSs needs only two parameters ( $\sigma_F$  and  $\sigma_R$ ). In the aforesaid analysis, the Malinowski's factor indicator function (IND) is used to deduce the number of factors.<sup>31</sup> The IND values associated with

one, two and three factors are 0.2545, 0.0555 and 0.0993, respectively. This shows that the minimum is reached when two factors are employed. By rotating the abstract factors to  $\sigma_F$ ,  $\sigma_R$  and  $\sigma_\alpha$ , it was found that the optimum combination with two factors was that of  $\sigma_F$  and  $\sigma_R$ . Hence the contribution of the third parameter ( $\sigma_\alpha$ ) to the correlation analysis can be neglected. However, for some groups which possess a large polarizability effect, e.g.  $\text{CH}_3\text{S}$ ,  $\text{SiMe}_3$ , Ph, vinyl and *t*-Bu, the contribution of the polarizability effect might also play a role in affecting the chemical shifts of Y-TFSs. In fact, if these groups are excluded in the dual parameter correlation, the goodness of fit of the correlation with  $\sigma_F$  and  $\sigma_R$  is improved. Therefore, our results suggest that although the polarizability effect is very small if all kinds of substituents are considered, it is not necessarily non-existent for molecules bearing substituents with large  $\sigma_\alpha$  values.

The field/inductive effect of substituents on  $^{19}\text{F}$  chemical shifts in substituted arene ring systems involves two electronic transmission mechanisms,<sup>32,33</sup> i.e. the field-induced polarization of the aromatic electron system and the direct field effect. Reynolds and Hamer<sup>32</sup> employed the internal shift differential ( $\Delta\delta_F = \delta_{F^1} - \delta_{F^2}$ ) of 4-substituted  $\beta,\beta$ -difluorostyrenes (6) to assess the direct electrostatic field effect. They pointed out that the direct field effect is negligible for  $\delta_{F^2}$  since the field acts almost at right-angles to the C—F<sup>2</sup> bond. If  $\rho_F$  in the DSP equation for  $\delta_{F^2}$  is assigned entirely to the field-induced  $\pi$ -polarization in 6, then the  $\rho_F$  for  $\delta_{F^1}$  may reflect the total of the two effects mentioned above. Thus, from the value (0.85) of the ratio  $\rho_F(\delta_{F^2})/\rho_F(\delta_{F^1})$  it was deduced that about 85% of the field/inductive effect for  $\delta_{F^1}$  is caused by  $\pi$ -polarization.<sup>32</sup> Adcock and Kok<sup>21</sup> also obtained similar results for 7, i.e. 89% polarization, 11% direct field effect. For our Y-TFS system, the ratio  $\rho_1(\delta_{F^2})/\rho_1(\delta_{F^1})$  is 0.82.

#### The unresolved polar substituent parameter $\sigma_{mb}$

At this juncture, we should establish whether any of the available unresolved  $\sigma^x$  scale can correlate well our  $^{19}\text{F}$  NMR data by a single parameter equation [equation (8)]. If any one of them does, then there is no need for a ' $\sigma_{mb}$ ' scale (see above). In fact, as might have been expected, among all other scales that had been tried, i.e.  $\sigma_p$ ,  $\sigma^0$ ,  $\sigma^-$ , etc., the  $\sigma^+$  scale gave the best fit by equation (8).

$$\text{Variable} = \rho^x \sigma^x + C \quad (8)$$

The  $\psi$  values for variables  $p\text{-}\Delta\delta_{3-1}$  and  $p\text{-}\Delta\delta_{3-2}$  given in Table 6 show that the correlation is not good enough compared with the dual parameter correlation tabulated previously (Table 2). This is expected, as discussed in our introductory remarks and previously,<sup>13</sup> because the mechanism of interaction between Y and the double

bond is different from that between Y and a carbocation if Y is in possession of  $\pi$ - and n-electrons. Indeed, Figure 1 shows that if  $\Delta\delta_{3-1}$  is plotted against  $\sigma^+$ , those groups which deviate most from the regression line are groups with  $\pi$ - or n-electrons, or with high polarizability.

Of particular interest, perhaps, is the fact that in our Y-TFS system both the *p*-vinyl and *p*-phenyl groups become electron sinks ( $\Delta\delta_{3-1}$  values 0.78 and 0.80) whereas their  $\sigma^+$  values suggest otherwise ( $\sigma^+$  values  $-0.16$ <sup>34</sup> and  $-0.18$ <sup>25</sup>). Further, our data show that  $\text{SiMe}_3$  is clearly an electron-withdrawing group, and  $\text{MeS}$  is much less electron-donating in the Y-TFS system.

The above observations suggest that it is justifiable to introduce another unresolved  $\sigma^x$  scale, viz.  $\sigma_{mb}$ , to be used in systems in which the substituent Y interacts with multiple bonds. In order to set our  $\sigma_{mb}$  scale comparable in magnitude to the  $\sigma^+$  scale, we define our  $\sigma_{mb}$  value by the equation

$$\sigma_{mb} = 0.16\Delta\delta_{3-1} - 0.09 \quad (9)$$

Actually, we had found that almost identical results would be obtained if we opted to use the  $\Delta\delta_{3-2}$  data instead of  $\Delta\delta_{3-1}$ . In equation (9), the coefficient is conveniently taken to be 0.16, the slope of the regression line in Figure 1. Twenty-seven values of  $\sigma_{mb}$  for *para* and *meta* substituents are presented in Table 7.

One of the persuasive reasons for presenting our  $\sigma_{mb}$  scale is the fact that those groups which deviate from the regression line of  $\Delta\delta_{3-1}$  vs  $\sigma^+$  plot because they are in possession of n- or  $\pi$ -electrons correlate very well with  $\sigma_{mb}$ , whereas with  $\sigma^+$  they do not. Comparisons of the correlations of some combinations of these groups with either  $\sigma^+$  or  $\sigma_{mb}$  are listed in Table 8. The results of comparing three substituent sets show that the  $\sigma_{mb}$  scale clearly performs better than the  $\sigma^+$  scale.

Therefore, we propose the  $\sigma_{mb}$  scale with the hope that it will be applicable to and useful in some systems which possess a multiple bond in conjugation with the aromatic ring. For instance, to serve as a first test of the applicability of the  $\sigma_{mb}$  scale, we may correlate Reynolds' data for styrene (5) and  $\beta,\beta$ -difluorostyrene

Table 6. Values of  $\rho^x$  of equation (8) and corresponding values of the correlation coefficient  $R$ , standard deviation  $s$  and  $\psi$  for correlation of  $^{19}\text{F}$  NMR of 20 Y-TFSs with substituent parameter  $\sigma^+$

Variable	$\rho^x$	$R$	$s$	$\psi$
<i>p</i> - $\delta_{F^1}$	$-3.63 \pm 0.27$	0.974	0.53	0.24
<i>p</i> - $\delta_{F^2}$	$-3.69 \pm 0.28$	0.971	0.57	0.25
<i>p</i> - $\delta_{F^3}$	$1.28 \pm 0.35$	0.675	0.88	0.78
<i>p</i> - $\Delta\delta_{3-1}$	$4.87 \pm 0.38$	0.950	1.00	0.33
<i>p</i> - $\Delta\delta_{3-2}$	$4.97 \pm 0.39$	0.946	1.07	0.34

(6). These correlations are designated as correlation As and are compared with Reynolds' dual-parameter ( $\sigma_F$  and  $\sigma_R^0$ ) correlation Bs in Table 9. Apparently, the two

correlations, A and B, are about equally satisfactory. We hope some other workers will find the  $\sigma_{mb}$  scale useful and applicable to their own studies.

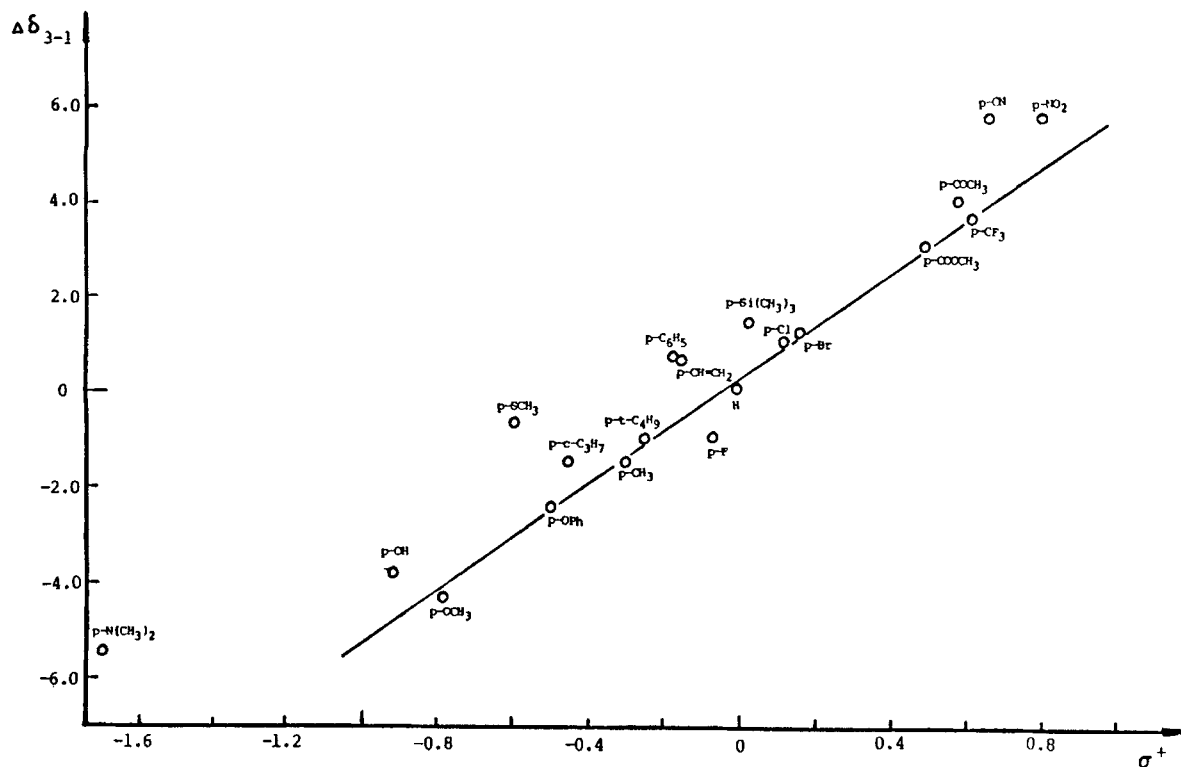


Figure 1. Plot of  $\Delta\delta_{3-1}$  versus  $\sigma^+$

Table 7.  $\sigma_{mb}$  values based on the  $^{19}\text{F}$  NMR chemical shifts of Y-TFS

Substituent	$\sigma_{mb}$	Substituent	$\sigma_{mb}$	Substituent	$\sigma_{mb}$
<i>p</i> -NMe <sub>2</sub>	-0.96	<i>p</i> -Vinyl	0.03	<i>m</i> -Me	-0.20
<i>p</i> -MeO	-0.77	<i>p</i> -Ph	0.04	<i>m</i> - <i>t</i> -Bu	-0.20
<i>p</i> -PhO	-0.46	<i>p</i> -Cl	0.11	<i>m</i> -Et	-0.15
<i>p</i> - <i>c</i> -Pr	-0.31	<i>p</i> -Br	0.13	<i>m</i> -MeO	-0.11
<i>p</i> -Me	-0.29	<i>p</i> -SiMe <sub>3</sub>	0.14	<i>m</i> -Cl	0.12
<i>p</i> -F	-0.24	<i>p</i> -COOMe	0.48	<i>m</i> -F	0.23
<i>p</i> - <i>t</i> -Bu	-0.22	<i>p</i> -CF <sub>3</sub>	0.49	<i>m</i> -Br	0.36
<i>p</i> -MeS	-0.18	<i>p</i> -COMe	0.56	<i>m</i> -CF <sub>3</sub>	0.39
H	0	<i>p</i> -CN	0.86		
		<i>p</i> -NO <sub>2</sub>	0.86		

Table 8. Comparison of the results of the correlation of  $\Delta\delta_{3-1}$  with  $\sigma^+$  and  $\sigma_{mb}$  by equation (8)

$\sigma^x$	<i>R</i>	<i>s</i>	$\psi$	<i>n</i>	Substituent set
$\sigma^+$	0.971	0.68	0.30	6	A = H, NMe <sub>2</sub> , MeS, Ph, Vinyl, Me <sub>3</sub> Si
$\sigma_{mb}$	0.996	0.25	0.11	6	A
$\sigma^+$	0.928	0.95	0.44	7	A plus F
$\sigma_{mb}$	0.996	0.23	0.11	7	A plus F
$\sigma^+$	0.928	1.30	0.43	8	A plus F and CN
$\sigma_{mb}$	0.998	0.22	0.07	8	A plus F and CN

Table 9. Comparison of the results of correlation A with correlation B for  $\beta,\beta$ -difluorostyrenes 7 ( $\delta_F^1$  and  $\delta_F^2$ ) and styrenes 6 ( $\delta_H^1$ ,  $\delta_H^2$ ,  $\delta_H^3$ ,  $\Delta\delta_{3-1}$  and  $\Delta\delta_{3-2}$ )

Variable	<i>R</i>		<i>s</i>		$\psi$		<i>n</i>
	A	B	A	B	A	B	
$\delta_F^1$	0.992	0.996	0.41	0.32	0.15	0.11	9
$\delta_F^2$	0.995	0.991	0.31	0.44	0.12	0.17	9
$\delta_H^1$	0.980	0.985	0.021	0.023	0.21	0.19	17
$\delta_H^2$	0.976	0.993	0.027	0.018	0.23	0.13	17
$\delta_H^3$	0.845	0.852	0.027	0.030	0.57	0.50	17
$\Delta\delta_{3-2}$	0.934	0.986	0.030	0.015	0.38	0.18	17
$\Delta\delta_{3-1}$	0.977	0.963	0.013	0.017	0.23	0.30	17

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