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### SYNTHESIS AND CHARACTERIZATION OF ARYL-2,2,2-TRIFLUOROETHYL SULFITES

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## SYNTHESIS AND CHARACTERIZATION OF ARYL-2,2,2-TRIFLUOROETHYL SULFITES

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Some new unsymmetrical aryl sulfites,  $\text{XC}_6\text{H}_4\text{OS(O)OCH}_2\text{CF}_3$  ( $\text{X} = \text{H}, p\text{-Cl}, p\text{-Me}, o\text{-Me}, o\text{-NO}_2$ ) are prepared and characterized by molecular spectroscopy (IR, Mass,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR). The  $^1\text{H}$  NMR chemical shift difference ( $\Delta\delta_{\text{H}_\text{A}\text{H}_\text{B}}$ ) of non equivalent  $\alpha$ -methylene protons depend on the nature and position of substituents in the phenyl ring.

**Key words:** Unsymmetrical sulfites, non-equivalence,  $\alpha$ -methylene protons, ring current.

### INTRODUCTION

Symmetrical organic sulfites have been extensively investigated because of their interesting structural features,<sup>1–4</sup> chemical reactivity<sup>5–8</sup> and multifarious practical applications.<sup>9–11</sup> The pivotal point in the structure analysis of these compounds has been the non-equivalence of  $\alpha$ -methylene protons.<sup>1–4</sup> However for unsymmetrical organic sulfites, such studies have been scanty. Recently, we have synthesized a few alkyl-2,2,2-trifluoroethyl sulfites,  $\text{RCH}_2\text{OS(O)OCH}_2\text{CF}_3$  and reported a detailed analyses of  $^1\text{H}$ NMR chemical shifts of non-equivalent  $\alpha$ -methylene protons.<sup>12</sup> It has been demonstrated for the first time that the bulk of alkyl substituent (R) affects the  $^1\text{H}$  NMR chemical shifts of protons of both the methylene groups present in the molecule. It is now considered appropriate to extend these studies to corresponding aryl derivatives. Thus some hitherto unknown unsymmetrical aryl sulfites such as  $\text{XC}_6\text{H}_4\text{OS(O)OCH}_2\text{CF}_3$  ( $\text{X} = \text{H}, p\text{-Cl}, p\text{-Me}, o\text{-Me}, o\text{-NO}_2$ ) are synthesized here and characterized. High resolution  $^1\text{H}$  NMR spectra of these compounds are discussed in relation to diastereotopicity of  $\alpha$ -methylene protons. The details are reported in this paper.

### EXPERIMENTAL

All manipulations were carried out in an atmosphere of dry nitrogen, using standard vacuum line techniques. Thionyl chloride (Fluka) was distilled over mercury prior to use. Phenol/*p*-chlorophenol/*p*-methylphenol/*o*-methylphenol/*o*-nitrophenol (E. Merck) were purified by standard methods.<sup>13</sup> 2,2,2-Trifluoroethyl alcohol (Fluka) was used as procured. Triethylamine (Aldrich) was refluxed over KOH pellets and distilled before use. Sulfur and chlorine were estimated by gravimetric methods.

Microanalyses of the samples were obtained using Perkin-Elmer (Model 2400) CHN Analyzer. Gas chromatographic analyses were performed as already reported.<sup>12</sup> IR spectra were routinely run as thin films/nujol mull using KBr optics on Perkin-Elmer 1430 ratio recording spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on Bruker AMX-400 instrument using TMS (for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei) and Freon-11 (for  $^{19}\text{F}$  nucleus) as standard references in  $\text{CDCl}_3$ . Mass spectra were recorded at 70 eV on VG analytical 70-S spectrometer.

### Preparative Methods

Phenyl/*p*-chlorophenyl/*p*-methylphenyl/2,2,2-trifluoroethyl chlorosulfites were prepared according to the reported procedure.<sup>8,14</sup> The identity of these compounds were checked by elemental analyses (Cl and S only), IR and <sup>1</sup>H NMR spectral data.

#### Phenyl/*p*-chlorophenyl/*p*-methylphenyl-2,2,2-trifluoroethyl Sulfites

A stirred solution of 2,2,2-trifluoroethanol (10.0 g, 7.3 mL, 0.1 mol) and triethylamine (10.0 g, 7.1 mL, 0.1 mol) in 50 mL dry diethylether was treated separately at -10°C with an equimolar amount of Phenyl/*p*-chlorophenyl/*p*-methylphenyl chlorosulfite, dissolved in 30 mL of the solvent. After the contents were refluxed for 6 h, triethylamine hydrochloride was filtered. The filtrate was fractionally distilled under reduced pressure using 2 ft long silvered glass column containing glass helices to afford the desired products XC<sub>6</sub>H<sub>4</sub>OS(O)OCH<sub>2</sub>CF<sub>3</sub> in 80–85% yield. B.P. (°C/mmHg): 90/2 for X = H, 85/2 for X = *p*-Cl, 78/2 for X = *p*-Me. Found: C, 40.2; H, 2.8; S, 13.6. Calc. for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S: C, 40.0; H, 2.9; S, 13.3%. Found: C, 34.9; H, 2.1; S, 11.8. Calc. for C<sub>8</sub>H<sub>6</sub>ClF<sub>3</sub>O<sub>3</sub>S: 34.7; H, 2.2; S, 11.7%. Found: C, 42.3; H, 3.5; S, 12.3. Calc. for C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>O<sub>3</sub>S: C, 42.5; H, 3.5; S, 12.6%.

#### *o*-Methylphenyl-2,2,2-trifluoroethyl Sulfite

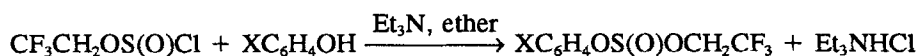
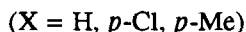
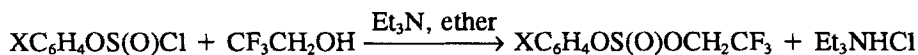
A mixture of *o*-methylphenol (10.5 g, 0.1 mol) and triethylamine (10.0 g, 7.1 mL, 0.1 mol) in dry diethylether (30 mL) was added dropwise into a stirred solution of 2,2,2-trifluoroethyl chlorosulfite (18.0 g, 0.1 mol) in the same solvent at -20°C. Thereafter, the contents were refluxed for 6 h. A similar work up procedure as described above was followed to obtain the desired compound. yield: 81%. B.P. (°C/mmHg): 70/2. Found: C, 42.4; H, 3.6; S, 12.4. Calc. for C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>O<sub>3</sub>S: C, 42.5; H, 3.5; S, 12.6%.

#### *o*-Nitrophenyl-2,2,2-trifluoroethyl Sulfite

The title compound was prepared by a similar procedure as described above for the *o*-methylphenyl derivative except that *o*-nitrophenol (14.0 g, 0.1 mol) was used as the starting reagent. The filtrate obtained after removal of triethylamine hydrochloride was concentrated and dry *n*-hexane was added to yield a yellow solid. Yield 84% m.p. 45°C. Found: C, 33.6; H, 2.1; N, 4.9; S, 11.2. Calc. for C<sub>8</sub>H<sub>6</sub>F<sub>3</sub>NO<sub>3</sub>S: C, 33.7; H, 2.1; N, 4.9; S, 11.2%.

## RESULTS AND DISCUSSION

The unsymmetric sulfites, XC<sub>6</sub>H<sub>4</sub>OS(O)OCH<sub>2</sub>CF<sub>3</sub> (X = H, *p*-Cl, *p*-Me) are prepared by the "Salt elimination" reactions between appropriate aryl chlorosulfite and 2,2,2-trifluoroethanol in the presence of triethylamine. However, *o*-methyl/*o*-nitrophenyl derivatives are obtained in good yields only by reacting 2,2,2-trifluoroethyl chlorosulfite and the corresponding substituted phenols in presence of the base. The reactions can be represented as follows:



These reactions generally take place under mild conditions and with quantitative conversion to the expected products with isolated yield ranging from 80 to 85%. All the compounds mentioned above (except the *o*-nitrophenyl derivative; mp 45°C) are

colorless distillable liquids and are obtained in 99% purity as evidenced by GLC analyses.

### Spectral Data

Infrared spectra of these compounds reveal important absorptions at 1285–1280, 1235–1220, 1180–1160, 940–830 and 550–530  $\text{cm}^{-1}$ , attributable to  $\nu_{\text{as}}\text{CF}_3$ ,  $\nu\text{S}=\text{O}$ ,  $\nu_s\text{CF}_3$ ,  $\nu\text{SO}(\text{C})$  and  $\delta\text{SO}_2$  modes respectively.<sup>2,12</sup> The vibrational modes for phenyl/substituted phenyl groups appear at 1590–1570, 1490–1480 and 790–760  $\text{cm}^{-1}$ .

Mass spectra of the above sulfites show a molecular ion peak  $[\text{M}]^+$  in each case (Table I). Similar to the spectra of alkyl-2,2,2-trifluoroethyl sulfites,<sup>12</sup> the aryl derivatives also undergo S—O bond cleavage resulting in the formation of ions such as  $[\text{X}-\text{C}_6\text{H}_4\text{OSO}]^+$ ,  $[\text{CF}_3\text{CH}_2\text{OSO}]^+$  and  $[\text{XC}_6\text{H}_4\text{O}]^+$ . As is apparent from the table, the resonance stabilized  $[\text{X}-\text{C}_6\text{H}_4\text{O}]^+$  fragment<sup>15</sup> is generally the prominent peak

TABLE I  
Mass spectral data of phenyl/*p*-chlorophenyl/*p*-methylphenyl/*o*-methylphenyl/*o*-nitrophenyl-2,2,2-trifluoroethyl sulfites

Fragment ion $m/z^*$ (% Base)	X-C <sub>6</sub> H <sub>4</sub> OS(O)OCH <sub>2</sub> CF <sub>3</sub>				
	X = H	X = <i>p</i> -Cl	X = <i>p</i> -CH <sub>3</sub>	X = <i>o</i> -CH <sub>3</sub>	X = <i>o</i> -NO <sub>2</sub>
$[\text{X}-\text{C}_6\text{H}_4\text{OS(O)CH}_2\text{CF}_3]^+$	240 (61.4)	274 (22.0) 276 (7.4)	254 (24.8)	254 (19.6)	285 (24.9)
$[\text{X}-\text{C}_6\text{H}_4\text{OCH}_2\text{CF}_3]^+$	176 (8.9)	210 (5.5)	190 (6.8)	190 (7.5)	221 (6.0)
$[\text{C}_6\text{H}_5\text{OCH}_2]^+$	107 (3.4)	—	—	—	—
$[\text{X}-\text{C}_6\text{H}_4\text{OSO}]^+$	141 (20.0)	175 (11.7)	155 (57.4)	155 (43.5)	—
$[\text{CF}_3\text{CH}_2\text{OSO}]^+$	147 (22.2)	147 (7.3)	147 (4.5)	147 (3.8)	147 (100.0)
$[\text{X}-\text{C}_6\text{H}_4\text{O}]^+$	93 (100.0)	127 (100.0) 129 (40.4)	107 (74.0)	107 (98.9)	—
$[\text{CF}_3\text{CH}_2]^+$	83 (27.4)	83 (22.2)	83 (7.2)	83 (7.5)	83 (74.2)
$[\text{CF}_3]^+$	69 (1.0)	69 (1.5)	—	—	69 (4.0)
$[\text{HSO}_2]^+$	65 (55.5)	65 (40.5)	65 (13.0)	65 (15.5)	65 (7.0)
$[\text{SO}_2]^+$	64 (4.3)	64 (16.3)	64 (3.0)	64 (4.2)	64 (18.0)
$[\text{SO}]^+$	48 (1.4)	48 (5.3)	48 (1.2)	48 (1.5)	48 (7.0)
$[\text{X}-\text{C}_6\text{H}_4]^+$	77 (27.2)	111 (14.2) 113 (3.9)	91 (100.0)	91 (100.0)	122 (39.9)

\* Mass numbers are based upon <sup>1</sup>H, <sup>12</sup>C, <sup>14</sup>N, <sup>16</sup>O, <sup>19</sup>F, <sup>32</sup>S, <sup>35</sup>Cl/<sup>37</sup>Cl. Values in parentheses denote % intensity of the fragments.

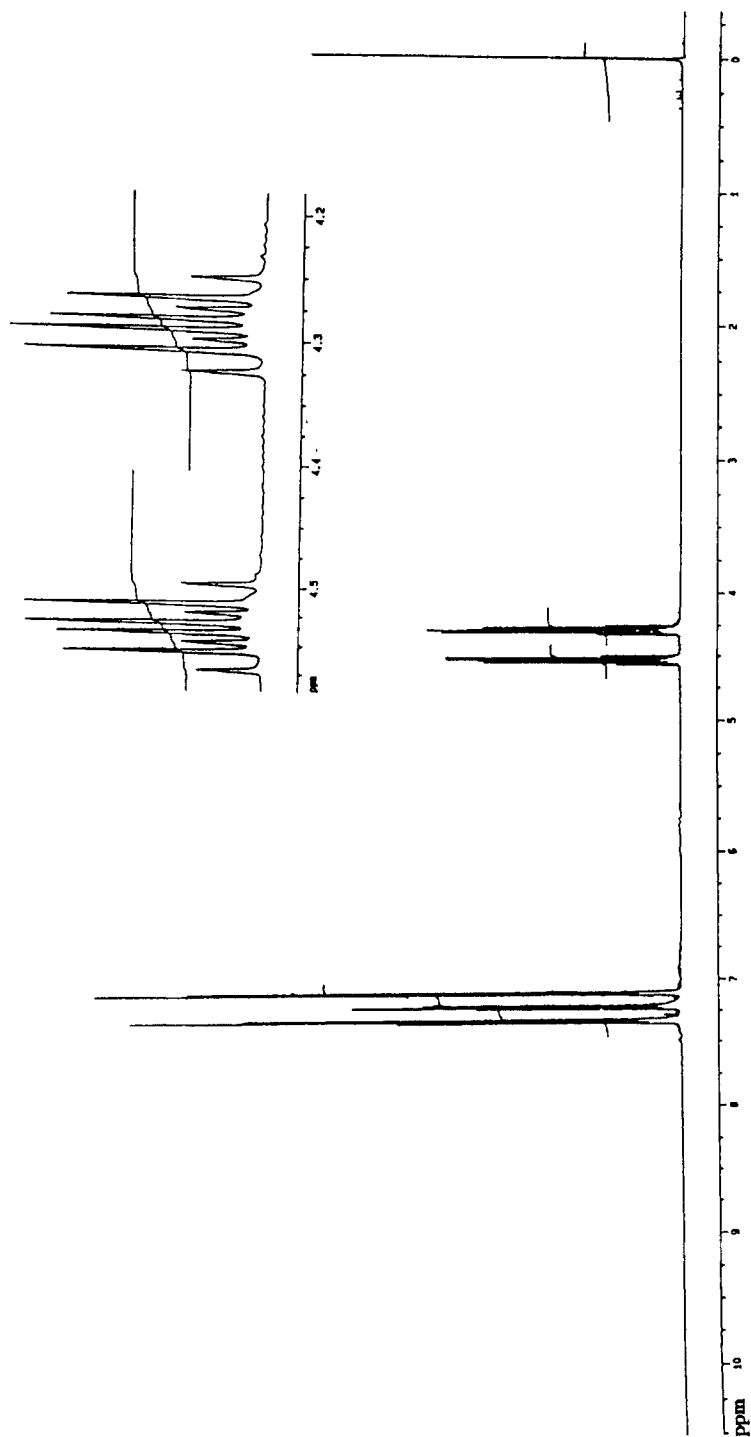


FIGURE 1  $^1\text{H}$  NMR splitting pattern for the  $\alpha$ -methylene protons of 2,2,2-trifluoroethyl group in  $\text{C}_6\text{H}_5\text{OS(O)OCH}_2\text{CF}_3$ .

TABLE II

<sup>1</sup>H NMR spectral data of phenyl/*p*-chlorophenyl/*p*-methylphenyl/*o*-methylphenyl/*o*-nitrophenyl-2,2,2-trifluoroethyl sulfites

Compound	Chemical shift* ( $\delta$ ), ppm	$\Delta\delta H_A H_B = [\delta H_B - \delta H_A]$ , (ppm)	$^nJ(H-H/F)$ , Hz
 <chem>OS(O)OCH2CF3</chem>	A = 4.287 (1H, dq) B = 4.534 (1H, dq) a = 7.110 (2H, d) b = 7.334 (2H, dt) c = 7.223 (1H, dt)	0.247	$^2J(H_A-H_B) = 12.4$ $^3J(H_A-F) = 8.2$ $^3J(H_B-F) = 8.4$
 <chem>OS(O)OCH2CF3</chem>	A = 4.339 (1H, dq) B = 4.553 (1H, dq) a = 7.051 (2H, dd) b = 7.309 (2H, dd)	0.214	$^2J(H_A-H_B) = 12.4$ $^3J(H_A-F) = 8.1$ $^3J(H_B-F) = 8.3$
 <chem>OS(O)OCH2CF3</chem>	A = 4.268 (1H, dq) B = 4.532 (1H, dq) a = 6.994 (2H, d) b = 7.124 (2H, d) c = 2.291 (3H, s)	0.264	$^2J(H_A-H_B) = 12.4$ $^3J(H_A-F) = 8.3$ $^3J(H_B-F) = 8.1$
 <chem>OS(O)OCH2CF3</chem>	A = 4.284 (1H, dq) B = 4.580 (1H, dq) a = 7.228 (1H, d) b = 7.142 (1H, dt) c = 7.212 (1H, dt) d = 7.095 (1H, dd) e = 2.286 (3H, s)	0.296	$^2J(H_A-H_B) = 12.4$ $^3J(H_A-F) = 8.1$ $^3J(H_B-F) = 8.3$
 <chem>OS(O)OCH2CF3</chem>	A = 4.504 (1H, dq) B = 4.705 (1H, dq) a = 8.019 (1H, dd) b = 7.446 (1H, dt) c = 7.684 (1H, dt) d = 7.349 (1H, dd)	0.201	$^2J(H_A-H_B) = 12.3$ $^3J(H_A-F) = 8.1$ $^3J(H_B-F) = 8.2$

\* A, B denotes non equivalent  $\alpha$ -methylene protons of  $-\text{OCH}_2\text{CF}_3$  group, while a, b, c, d, e are ascribed to different hydrogen atoms as specified.

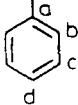
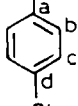
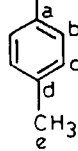
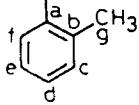
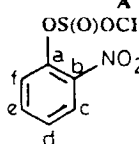
TABLE III

Variable temperature <sup>1</sup>H NMR spectral data of *o*-nitrophenyl-2,2,2-trifluoroethyl sulfite

Temp., (K)	Chemical shift* ( $\delta$ ), ppm						$\Delta\delta H_A H_B$ , ppm	$^nJ(H-H/F)$ , Hz
	A	B	a	b	c	d		
323	4.474 (1H, dq)	4.673 (1H, dq)	8.003 (1H, dd)	7.416 (1H, dt)	7.648 (1H, dt)	7.332 (1H, dd)	0.199	$^2J(H_A-H_B) = 12.3$ $^3J(H_A-F) = 8.0$ $^3J(H_B-F) = 8.2$
303	4.490 (1H, dq)	4.690 (1H, dq)	8.002 (1H, dd)	7.435 (1H, dt)	7.668 (1H, dt)	7.339 (1H, dd)	0.200	$^2J(H_A-H_B) = 12.3$ $^3J(H_A-F) = 8.0$ $^3J(H_B-F) = 8.2$
293	4.497 (1H, dq)	4.696 (1H, dq)	8.029 (1H, dd)	7.445 (1H, dt)	7.678 (1H, t)	7.342 (1H, d)	0.199	$^2J(H_A-H_B) = 12.4$ $^3J(H_A-F) = 8.1$ $^3J(H_B-F) = 8.1$
273	4.528 (1H, dq)	4.728 (1H, dq)	8.056 (1H, d)	7.480 (1H, t)	7.717 (1H, t)	7.339 (1H, d)	0.200	$^2J(H_A-H_B) = 12.3$ $^3J(H_A-F) = 7.9$ $^3J(H_B-F) = 8.1$

\* All notations given above have the same meaning as illustrated in Table II.

TABLE IV  
 $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectral data of phenyl/*p*-chlorophenyl/*p*-methylphenyl/*o*-methylphenyl/  
*o*-nitrophenyl-2,2,2-trifluoroethyl sulfites

Compound	Chemical shift* ( $\delta^{13}\text{C}$ ), † ppm	$^nJ(^{13}\text{C}-^{19}\text{F})$ , Hz	Chemical shift ( $\delta^{19}\text{F}$ ), ppm	$^nJ(^{19}\text{F}-\text{H})$ , Hz
<p><b>A B</b></p> <p>OS(O)OCH<sub>2</sub>CF<sub>3</sub></p> 	<p>A = 56.9 (q)</p> <p>B = 123.1 (q)</p> <p>a = 149.1 (s)</p> <p>b = 121.9 (s)</p> <p>c = 130.5 (s)</p> <p>d = 127.1 (s)</p>	<p><math>^1J(^{13}\text{C}-^{19}\text{F}) = 277.5</math></p> <p><math>^2J(^{13}\text{C}-^{19}\text{F}) = 37.8</math></p>	-73.5 (t)	$^3J(^{19}\text{F}-\text{H}) = 8.2$
<p><b>A B</b></p> <p>OS(O)OCH<sub>2</sub>CF<sub>3</sub></p> 	<p>A = 57.2 (q)</p> <p>B = 122.9 (q)</p> <p>a = 147.4 (s)</p> <p>b = 123.4 (s)</p> <p>c = 130.1 (s)</p> <p>d = 117.1 (s)</p>	<p><math>^1J(^{13}\text{C}-^{19}\text{F}) = 277.5</math></p> <p><math>^2J(^{13}\text{C}-^{19}\text{F}) = 37.9</math></p>	-73.0 (t)	$^3J(^{19}\text{F}-\text{H}) = 8.2$
<p><b>A B</b></p> <p>OS(O)OCH<sub>2</sub>CF<sub>3</sub></p> 	<p>A = 56.8 (q)</p> <p>B = 123.2 (q)</p> <p>a = 146.7 (s)</p> <p>b = 121.8 (s)</p> <p>c = 130.9 (s)</p> <p>d = 136.9 (s)</p> <p>e = 20.9 (s)</p>	<p><math>^1J(^{13}\text{C}-^{19}\text{F}) = 277.2</math></p> <p><math>^2J(^{13}\text{C}-^{19}\text{F}) = 37.8</math></p>	-73.2 (t)	$^3J(^{19}\text{F}-\text{H}) = 8.3$
<p><b>A B</b></p> <p>OS(O)OCH<sub>2</sub>CF<sub>3</sub></p> 	<p>A = 56.9 (q)</p> <p>B = 122.8 (q)</p> <p>a = 147.8 (s)</p> <p>b = 127.7 (s)</p> <p>c = 132.1 (s)</p> <p>d = 122.0 (s)</p> <p>e = 127.1 (s)</p> <p>f = 120.9 (s)</p> <p>g = 16.7 (s)</p>	<p><math>^1J(^{13}\text{C}-^{19}\text{F}) = 277.3</math></p> <p><math>^2J(^{13}\text{C}-^{19}\text{F}) = 37.8</math></p>	-73.2 (t)	$^3J(^{19}\text{F}-\text{H}) = 8.2$
<p><b>A B</b></p> <p>OS(O)OCH<sub>2</sub>CF<sub>3</sub></p> 	<p>A = 57.9 (q)</p> <p>B = 122.9 (q)</p> <p>a = 143.2 (s)</p> <p>b = 142.1 (s)</p> <p>c = 126.4 (s)</p> <p>d = 127.5 (s)</p> <p>e = 135.2 (s)</p> <p>f = 125.6 (s)</p>	<p><math>^1J(^{13}\text{C}-^{19}\text{F}) = 277.5</math></p> <p><math>^2J(^{13}\text{C}-^{19}\text{F}) = 37.9</math></p>	-73.5 (t)	$^3J(^{19}\text{F}-\text{H}) = 8.2$

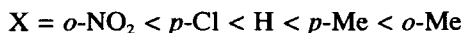
\* A, B and a, b, c, d, e, f, g denote different carbon atoms as specified.

† Solvent CDCl<sub>3</sub> ( $\delta^{13}\text{C} = 77.5$  ppm).

in the spectra of all these compounds except in the *o*-nitrophenyl derivative where  $[\text{CF}_3\text{CH}_2\text{OSO}]^+$  is the most dominant one.

High resolution  $^1\text{H}$ -NMR spectrum of each compound in CDCl<sub>3</sub> reveals two distinct sets of multiplets of ABX<sub>3</sub> spin system in the region 5.0–4.5 and 4.4–4.0 ppm (Figure 1). In accord with the known structural features of organic sulfites,<sup>2,12</sup> the observed spectral pattern can be attributed to the non-equivalent  $\alpha$ -methylene protons ( $\text{H}_\text{A}$ ,  $\text{H}_\text{B}$ ) of OCH<sub>2</sub>CF<sub>3</sub> group. The relevant spectral data are recorded in Table II. The chemical shift values of  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  protons are assigned according to the reported trends.<sup>12,16</sup> The chemical shift difference ( $\Delta\delta\text{H}_\text{A}\text{H}_\text{B} = \delta(\text{H}_\text{B}-\text{H}_\text{A})$ ) of the non-equivalent

$\alpha$ -methylene protons are observed in the range 0.201–0.296 ppm. The order of  $\Delta\delta_{H_A H_B}$  values as a function of X is as follows:



$$\Delta\delta_{H_A H_B} = 0.201 \ 0.214 \ 0.247 \ 0.264 \ 0.296 \ (\text{ppm})$$

A perusal of the above order reveals that chemical shift difference decreases with increase in electronegativity of the substituted phenyl ring. Steric effect of the aryl group does not seem to be important. This is evident as  $\Delta\delta_{H_A H_B}$  for phenyl group lies in the middle of the above series though sterically the phenyl group should be least effective in the molecule.

Variable temperature  $^1\text{H}$  NMR spectral data of *o*-nitrophenyl-2,2,2-trifluoroethyl sulfite recorded between 323–273 K (Table III) reveal that there is no meaningful change in the  $\Delta\delta_{H_A H_B}$  ( $0.200 \pm 0.001$  ppm) as well as in coupling constant  $^2J(H_A - H_B) = 12.4 \pm 0.1$  Hz values in this temperature range. These values are also similar in dilute (0.15 and 0.05 M) solutions too. These observations may indicate that chemical shifts of the methylene protons are predominantly influenced by intramolecular interaction. A comparison of the chemical shift difference data reported herein with those of previously known benzyl benzene sulfinate (0.501 ppm) and dibenzyl sulfites (0.115–0.129 ppm)<sup>18</sup> may suggest the dominant role of diamagnetic “ring current”<sup>19,20</sup> in the anisochronism of  $\alpha$ -methylene protons in the title unsymmetric aryl 2,2,2-trifluoroethyl sulfites.

$^{13}\text{C}$  and  $^{19}\text{F}$  NMR chemical shifts and coupling constant data (Table IV) are consistent with the structure of these compounds.<sup>2,21</sup>

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#### REFERENCES

1. J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).
2. R. A. De Marco, A. T. Kovacina and W. B. Fox, *J. Fluorine Chem.*, **5**, 221 (1975).
3. J. G. Tillett, *Int. J. Sulfur Chem.*, **3**, 289 (1973); *Chem. Abstr.*, **79**, 136013v (1973).
4. A. J. Baines and B. J. Vander Veken, *J. Mol. Struct.*, **157**, 119 (1987).
5. R. C. Kumar, S. A. Kinkad and J. M. Shreeve, *Inorg. Chem.*, **23**, 3112 (1984).
6. C. G. Krespan and B. E. Smart, *J. Org. Chem.*, **51**, 320 (1986).
7. Y. Tamaru, K. Nagao, T. Bando and Z. Yoshida, *J. Org. Chem.*, **55**, 1823 (1990).
8. H. F. Van Woerden, *Chem. Rev.*, **63**, 557 (1963).
9. E. Plichta, M. Salomon, S. Slane and M. Uchiyama, *J. Solution Chem.*, **15**, 663 (1986).
10. R. A. Covey and R. E. Grahame, Ger. Patent, 453138 (1975); *Chem. Abstr.*, **83**, 131317 v (1975).
11. Asahi Chemical Industry Co. Ltd., Jpn. Patent, 8,126,906 (1981); *Chem. Abstr.*, **95**, 43957w (1981).
12. S. P. Narula, S. Kaur, R. Shankar and S. K. Sharma, *Polyhedron*, **12**, 2447 (1993).
13. J. A. Riddick, W. B. Bunger and T. K. Sakano, “Techniques of Chemistry,” *Organic Solvents*, Vol. 2, 4th Edn., Wiley Interscience, New York, 1986.
14. R. A. De Marco, A. T. Kovacina and W. B. Fox, *J. Fluorine Chem.*, **6**, 93 (1975).
15. R. M. Silverstein, G. C. Bassler and T. C. Morrill, “Spectrometric Identification of Organic Compounds,” 5th Edn., John Wiley and Sons, New York, p. 15, 1991.
16. H. Finegold, *J. Phys. Chem.*, **72**, 3244 (1968).
17. A. G. Yurchenko, P. A. Krasutskii, A. N. Vlasova and Kh. E. Dzhuva, *Ser. Khim. Mashinobudov. Tekhnol.*, **14**, 15 (1977); *Chem. Abstr.*, **89**, 107104b (1978).



18. M. Oki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **35**, 1428 (1962).
19. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, p. 180, 1959.
20. C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
21. H. O. Kalinowski, S. Berger and S. Braun, "Carbon  $^{13}\text{NMR}$  Spectroscopy," John Wiley and Sons, New York, p. 326, 1988.