Journal of Fluorine Chemistry 131 (2010) 433–438

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

One-pot synthesis of arylfluoroalkylsulfoxides and study of their anomalous ^{19}F NMR behavior

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ARTICLE INFO

Article history:
Received 7 December 2009
Received in revised form 19 December 2009
Accepted 23 December 2009
Available online 4 January 2010

Keywords:
Arylfluoroalkylsulfoxides
Polyfluoroalkylsulfinylation
Chemical shifts
Coupling constants
Diastereotopic

ABSTRACT

Arylfluoroalkylsulfoxides were successfully synthesized in one-pot when fluoroalkylsulfinate reacted with benzene and triflic anhydride in triflic acid and dichloromethane as the medium. The characteristics of their ^{19}F NMR spectra were examined and analyzed for these structures. Electronic and steric effects of substituents at α- or β-position were revealed to be the main cause of the anomalous behavior of their chemical shifts and coupling constants. Interactions between arylfluoroalkylsulfoxides and solvents were also investigated and discussed.

1. Introduction

Introducing fluorine-containing groups into organic compounds and materials has attracted great interest in different fields of chemistry such as material science, biochemistry, pharmaceuticals and coordination chemistry. The fluorine-containing substituents often conferred unusual physical properties and enhanced chemical reactivities [1–4]. For example, the introduction of trifluoromethanesulfinyl group into benzene resulted in *S*-(trifluoromethyl)-diphenylsulfonium triflates with significantly different properties and applications from its precursor [5–9]. Little work on arylfluoroalkylsulfoxides has been available in the literature, however. These fluorinated sulfoxides were usually synthesized by the oxidation of corresponding sulfides with peracids, a process that is hard to control because a mixture of sulfoxide and sulfone compounds plus the initial sulfide was often obtained. In 2001, Wakselman et al. reported that aryltrifluoromethyl sulfoxides could directly be yielded from substituted benzenes and triflinates in the triflic acid medium [10]. Nevertheless, the preparation of other kinds of arylfluoroalkyl sulfoxides by this method is still undocumented. Aryl(iododifluoromethyl)sulfoxides, the first optically active compounds with polyfluoroalkyliodo groups, synthesized by Yagupolskii and Matsnev exhibited characteristic ^{19}F NMR spectra [11]. Chirality of the S=O group causes marked differences in chemical shift between the two gem-fluorine atoms. We report herein an improved procedure for the synthesis of arylfluoroalkylsulfoxides and examine the ^{19}F NMR spectra of the variously substituted fluoroalkylsulfoxides.

2. Results and discussion

The introduction of a trifluoromethanesulfinyl group into organic compounds using trifluoromethanesulfinyl chloride, or sodium trifluoromethanesulfinate and phosphoryl chloride, suffers from a low conversion efficiency problem due to the poor stability and low reactivity of these reagents [12–14]. Wakselman et al. consequently improved the method through the preparation of aryltrifluoromethyl sulfoxides from substituted benzenes and triflinates in the triflic acid medium [10]. Triflic anhydride and triflic acid were employed as activated reagents instead of commonly used acyl chloride or phosphoryl chloride. According to the literature, this method was effective for trifluoromethanesulfinylation of substituted aromatic compounds [10]. Application of this method to benzene itself, however, resulted in polymeric reactions. It was found that when sodium 2-chloro-1,1,2,2-tetrafluoroethanesulfinate reacted with benzene and triflic anhydride in triflic acid at room temperature, the system became ineffectual. ^{19}F NMR analyses of the reaction mixture showed the formation of undesired polyarylenesulfonium salts [15–17]. The yield of 1-(2-chloro-1,1,2,2-tetrafluoroethylsulfinyl)benzene (**1d**) was only 20% after 23 h, although the polyfluoroalkylsulfinate salt

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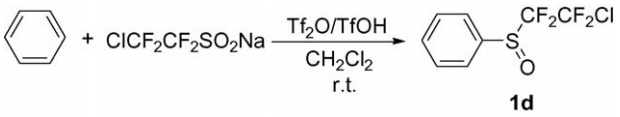
doi:10.1016/j.jfluchem.2009.12.019

Table 1
Preparation of 1-(2-chloro-1,1,2,2-tetrafluoroethylsulfinyl)benzene (**1d**)



Entry	R_fSO_2Na:Tf_2O:TfOH	Time (h)	Solvent	Yield[a] (%)
1	1:1.1:10	23	–	20
2	1:1.1:10	38	CH_2Cl_2	30
3	1:0:10	67	CH_2Cl_2	Trace
4	1:1.0:2.2	67	CH_2Cl_2	0

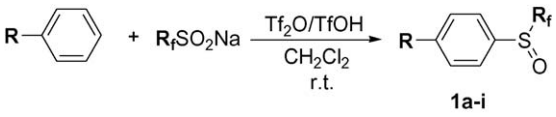
[a] Isolated yield.

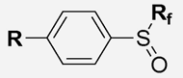
was completely consumed (entry 1, Table 1). To optimize the reaction system, dichloromethane was added as part of the medium. It was found that the polymerization reaction was efficiently inhibited, giving **1d** in 30% yield (entry 2, Table 1). However, longer reaction time was needed under this reaction condition. The polyfluoroalkylsulfinylation was also tremendously influenced by the amount of Tf_2O and TfOH. Only trace of **1d** was detected if no triflic anhydride was added at room temperature (entry 3, Table 1). Sufficient TfOH was necessary for the formation of **1d** (entry 4, Table 1).

In order to investigate the applicability of this method, we extended the reaction to the synthesis of other arylfluoroalkylsulfoxides. 1-(difluoromethylsulfinyl)benzene (**1a**) was prepared in 44% yield after 19 h from sodium difluoromethanesulfinate and benzene using triflic acid and dichloromethane as medium (entry 1, Table 2). Similar results were obtained in the case of sodium bromodifluoromethanesulfinate and sodium perfluoroethylsulfinate (entries 2 and 3, Table 2). With increased length of the polyfluoroalkyl chain, polyfluoroalkylsulfinylation reactions between benzene and polyfluoroalkylsulfinate were also successful, giving the desired sulfoxides **1e**, **1f** and **1g** in moderate yield (entries 5–7, Table 2). When diphenyl was employed as the substrate, the reaction stopped at the monofluoroalkylsulfinylation stage, giving para-substituted **1h** and **1i** as the only product (entries 8 and 9, Table 2). However, no sulfinylated product was observed in the case of terphenyl (entry 10, Table 2), as confirmed by ^{19}F NMR.

The chemical shift and coupling constant of CF_2 adjacent to the S=O group were dramatically influenced by its substituents. For example, the two fluorine nuclei of the CF_2 group in **1a** both appeared upfield at −119.1 ppm and the ones in **1b** shifted to downfield at −52.9 and −54.9 ppm, respectively (Fig. 1), indicating that the fluorine nuclei were sharply deshielded by the bromine atom at α-position in **1b** [18]. Further investigations showed that geminal coupling constants between the two fluorine atoms in **1a** and **1b** are markedly different. The chiral nature of the S=O group makes a favorable diastereotopic environment for the two fluorine atoms to differentiate, leading to that the two diastereotopic fluorines in **1b** possess larger observed geminal coupling constants

Table 2
Polyfluoroalkylsulfination of aromatic compounds



Entry	R	R_fSO_2Na		Time (h)	Yield[a] (%)
1	H	HCF_2	**1a**	19	44
2	H	$BrCF_2$	**1b**	19	28
3	H	CF_3CF_2	**1c**	36	37
4	H	$ClCF_2CF_2$	**1d**	38	30
5	H	$C_3H_3N_2CF_2CF_2$[b]	**1e**	41	60
6	H	$PhOCF_2CF_2$	**1f**	41	35
7	H	$ClCF_2CF_2CF_2CF_2$	**1g**	25	41
8	Ph	HCF_2	**1h**	10	21
9	Ph	$ClCF_2CF_2$	**1i**	30	34
10[c]	4-PhC_6H_4	$ClCF_2CF_2$	–	23	–

[a] Isolated yield.
[b] Sodium 1,1,2,2-tetrafluoro-2-(1H-imidazol-1-yl)ethanesulfinate.
[c] Determined by ^{19}F NMR.

than those in **1a** (Fig. 1). The bromine atom attached directly to CF_2 makes the two gem-fluorine atoms so different that the $^2J_{FF}$ coupling constant is raised to 145.3 Hz for **1b** compared to $^2J_{FF}$ = 5.1 Hz for **1a**. This is also the reason that the chemical shift of one fluorine atom in **1b** is −52.9 ppm and the other −54.9 ppm.

As shown in Fig. 2, when the fluorinated carbon was attached to the α-CF_2 group, large differences up to 11 ppm in chemical shift between the two diastereotopic fluorines at the α-position adjacent to the S=O group were observed in **1c–f**. For example, in **1c**, the chemical shifts for the two α-CF_2 fluorine nuclei were −115.6 and −126.1 ppm, respectively. Substitution with a weaker electronegative species relative to fluorine atoms at the β-position has a mild deshielding impact on the α-CF_2 group. For example, when the $ClCF_2$ group instead of CF_3 was employed to bond to α-CF_2, the chemical shift of α-CF_2 moved to the lower field (−109.7 and −121.9 ppm). Similar results were also found in **1e** and **1f**. As was the case in **1b**, stronger electronegative substituents at the β-position greatly deshielded the two β-CF_2 fluorine nuclei, leading to lower field in chemical shift (**1d–f** in Fig. 2). Chlorine displayed the largest deshielding effect compared to phenoxyl and imidazolyl function groups in these systems. But unnoticeable difference was observed in chemical shift between the two fluorine nuclei at the β-position in **1d–f**. This may be resulted from the longer distance between the fluorine nuclei and the optically active S=O group. A sulfinyl group was difficult to create diastereotopic environments for the two fluorine nuclei at β-position (**1d**). The steric effect which strengthens the diastereotopic environments of the fluorine nuclei by phenoxyl group and imidazolyl function was also substantially weakened by the increased spacious separation between the fluorine nuclei and the S=O group. As a result, only

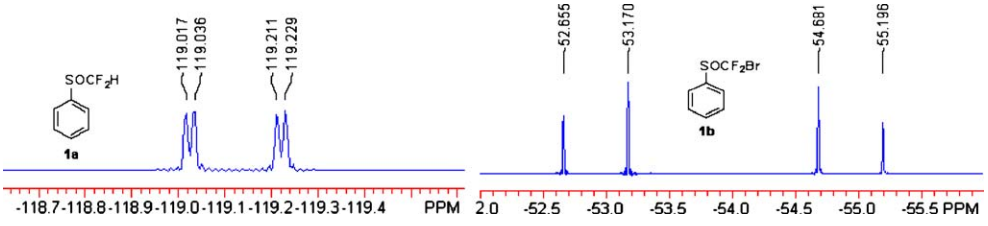
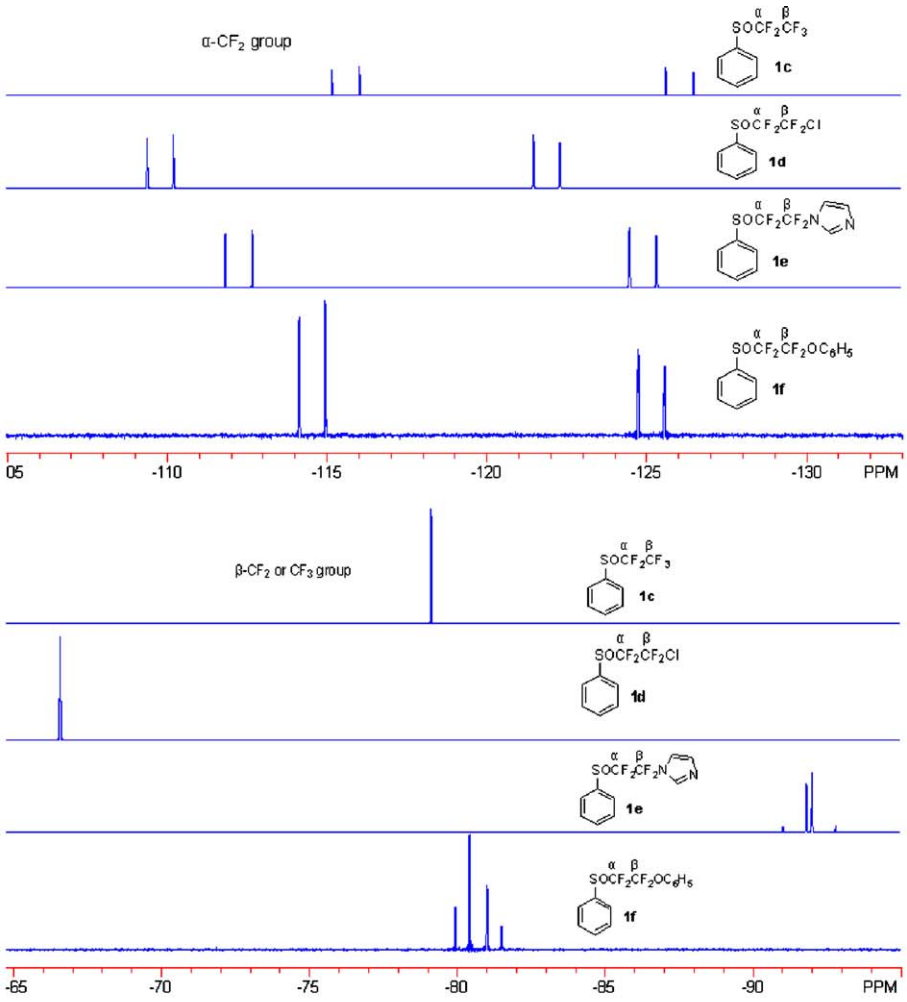


Fig. 1. ^{19}F NMR spectra of the CF_2 group in **1a** and **1b** in $CDCl_3$ (282 MHz).



1c: δ -79.1 (s, 3F), -115.6 (d, $^{2}J_{FF}$ = 243.3 Hz, 1F), -126.1 (d, $^{2}J_{FF}$ = 243.3 Hz, 1F).

1d: δ -66.6 (dd, $^{3}J_{FF}$ = 5.1 Hz, $^{3}J_{FF}$ = 4.5 Hz, 2F), -109.8 (dm, $^{2}J_{FF}$ = 233.0 Hz, 1F), -121.9 (dt, $^{2}J_{FF}$ = 233.0 Hz, $^{3}J_{FF}$ = 5.1 Hz, 1F).

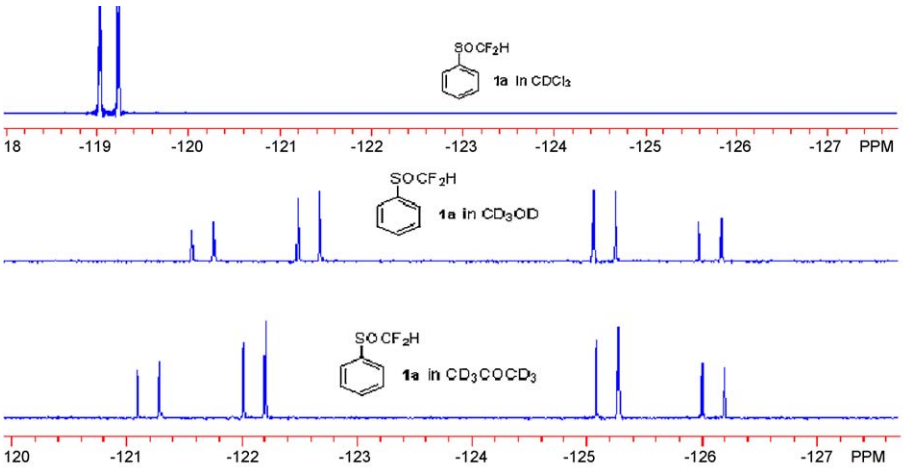
1e: δ -91.4 (dd, $^{2}J_{FF}$ = 227.9 Hz, $^{3}J_{FF}$ = 6.1 Hz, 1F), -92.4 (dd, $^{2}J_{FF}$ = 227.9 Hz, $^{3}J_{FF}$ = 3.1 Hz, 1F), -112.2 (d, $^{2}J_{FF}$ = 240.2 Hz, 1F), -124.9 (dd, $^{2}J_{FF}$ = 240.2 Hz, $^{3}J_{FF}$ = 6.1 Hz, 1F).

1f: δ -80.2 (dd, $^{2}J_{FF}$ = 141.2 Hz, $^{3}J_{FF}$ = 8.3 Hz, 1F), -81.2 (ddd, $^{2}J_{FF}$ = 141.2 Hz, $^{3}J_{FF}$ = 5.1 Hz, $^{3}J_{FF}$ = 4.1 Hz, 1F), -114.5 (dd, $^{2}J_{FF}$ = 232.0 Hz, $^{3}J_{FF}$ = 8.3 Hz, 1F), -125.1 (ddd, $^{2}J_{FF}$ = 232.0 Hz, $^{3}J_{FF}$ = 5.1 Hz, $^{3}J_{FF}$ = 4.1 Hz, 1F).

Fig. 2. ^{19}F NMR spectra of the α-CF_2 group and the β-CF_2 or CF_3 group in **1c–f** in $CDCl_3$ (282 MHz).

1 ppm difference of β-fluorine atoms in chemical shift was determined in **1e** and **1f**. In addition, coupling constants of the fluorine nuclei at both α- and β-positions were quite specific in **1c–f**. As shown in Fig. 2, geminal coupling constants between the two diastereotopic fluorines at the α-position for all these compounds were between 230 and 245 Hz whereas the range of $^{2}J_{FF}$ coupling constants between the two fluorine nuclei at the β-position was from 0 to 230 Hz. $^{3}J_{FF}$ coupling constants for diastereotopic fluorine nucleus between α- and β- positions in these compounds were also significantly distinguished. To the best of our knowledge, vicinal F–F coupling constants were mainly dictated by torsional angles between the coupled nuclei. A Karplus-type dependence of F–F three-bond coupling constants on the dihedral angle between the coupling nuclei was confirmed empirically by Williamson et al. [19]. Functional and steric groups at the β-position in **1d–f** were assumed to determine the optimal conformation of these fluorine atoms. Different values of the optimal dihedral angles between the coupled fluorine nuclei were simultaneously ascertained. These optimal conformations would further restrict the transformation of dihedral angle and thus lead to the coupled fluorine nucleus having the characteristic coupling constants in ^{19}F NMR spectra [18]. Similar analysis can be made about the chemical shift and coupling constants for other fluoroalkylsulfoxides such as **1g–i** and the same conclusions can be drawn.

We have however observed variations in fluorine chemical shifts and coupling constants for these typical compounds especially for **1a** and **1h**, in different solvents such as $CDCl_3$, CD_3OD and acetone-d_6. Taking **1a** as an example, we found that



In $CDCl_3$: δ -119.1 (dd, $^2J_{HF}$ = 55.8 Hz, $^2J_{FF}$ = 5.1 Hz, 2F)

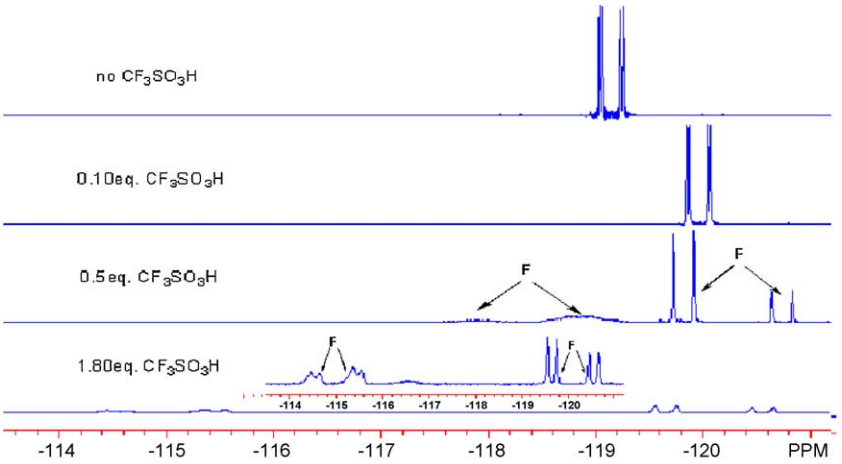
In CD_3OD: δ -122.1 (dd, $^2J_{HF}$ = 53.5 Hz, $^2J_{FF}$ = 259.6 Hz, 1F), -125.6 (dd, $^2J_{HF}$ = 53.5 Hz, $^2J_{FF}$ = 259.6 Hz, 1F)

In CD_3COCD_3: δ -121.7 (dd, $^2J_{HF}$ = 53.5 Hz, $^2J_{FF}$ = 260.6 Hz, 1F), -125.6 (dd, $^2J_{HF}$ = 53.5 Hz, $^2J_{FF}$ = 260.6 Hz, 1F)

Fig. 3. ^{19}F NMR spectra of **1a** in different solvents.

variations in fluorine chemical shifts for these three solvents were enormous, as shown in Fig. 3. The chemical shift for **1a** in $CDCl_3$ was −119.1 ppm with the geminal $^2J_{FF}$ coupling constant 5.1 Hz. But in CD_3OD the same quantities were found to be −122.1 and −125.6 ppm, respectively, with the $^2J_{FF}$ coupling constant of 259.6 Hz. The larger difference in chemical shift between the two fluorine nuclei of the same compound was also observed in CD_3COCD_3. One of the fluorine nuclei appeared at −121.7 ppm, in a little lower field than that in CD_3OD. These results indicate that the solvent effect as well as the hydrogen bond of **1a** with different solvent molecules seriously differentiates the diastereotopic environments of the two fluorine nuclei and intensifies the difference in chemical shift and coupling constants between the fluorine atoms.

In addition, the chemical shift and $^2J_{FF}$ coupling constant of **1a** in $CDCl_3$ were also affected by the addition of triflic acid. As shown in Fig. 4, the ^{19}F NMR spectrum of **1a** in $CDCl_3$ with the addition of CF_3SO_3H (0.10 equiv.) exhibited higher upfield signals than the one



No CF_3SO_3H in CD_3Cl: δ -119.1 (dd, $^2J_{HF}$ = 55.8 Hz, $^2J_{FF}$ = 5.1 Hz, 2F)

0.10eq. CF_3SO_3H in CD_3Cl: δ -119.9 (dd, $^2J_{HF}$ = 55.6 Hz, $^2J_{FF}$ = 5.7 Hz, 2F)

0.50eq. CF_3SO_3H in CD_3Cl: δ -118.4 (dbr, $^2J_{FF}$ = 259.9 Hz, 1F), -120.3 (dd, $^2J_{HF}$ = 55.7 Hz, $^2J_{FF}$ = 259.9 Hz, 1F)

1.80eq. CF_3SO_3H in CD_3Cl: δ -115.0 (dd, $^2J_{HF}$ = 57.7 Hz, $^2J_{FF}$ = 254.7 Hz, 1F), -120.1 (dd, $^2J_{HF}$ = 55.7 Hz, $^2J_{FF}$ = 254.7 Hz, 1F)

Fig. 4. ^{19}F NMR spectra of **1a** in $CDCl_3$ with CF_3SO_3H.

without CF_3SO_3H in the same solvent. In this case, almost the same $^2J_{FF}$ coupling constants were obtained. When the amount of triflic acid was increased to 0.50 equiv., a doublet of doublets at −120.3 ppm with the geminal F–F coupling of 259.9 Hz as well as two-bond H–F coupling of 55.7 Hz from one fluorine and a broad doublet at −118.4 ppm with two-bond F–F coupling from the other fluorine were seen. The diastereotopic environment for each of the two fluorine nuclei could further be altered by increasing the amount of CF_3SO_3H. About 5 ppm of difference between the two fluorine nuclei in chemical shift was found when 1.80 equiv. of CF_3SO_3H was added into $CDCl_3$. The $^2J_{FF}$ and $^2J_{HF}$ coupling constants for the fluorine nucleus moving downfield to −115.0 ppm were observed, exhibiting a doublet of doublets in its ^{19}F NMR spectrum. These results led us further to suggest that the solvent effect and the hydrogen bond interaction could markedly differentiate the two fluorine nuclei adjacent to the diastereotopic S=O group.

3. Conclusion

In conclusion, in the present work, we have developed an improved method for the synthesis of arylpolyfluoroalkylsulfoxides. With fluoroalkylsulfinates reacting with benzene and triflic anhydride in triflic acid and dichloromethane as the medium, this method enables us to prepare various arylfluoroalkylsulfoxide compounds in one-pot. Meanwhile, ^{19}F NMR spectrum features of these new compounds were carefully examined and analyzed. Electronic and steric effects of substituents at α- or β-position were identified to be the main cause of the different behavior in chemical shift and coupling constants. Interactions between substrates and solvents were also found to play an important role in their anomalous ^{19}F NMR behavior. Further studies on the nature of these effects from both experimental and computational perspectives are in progress.

4. Experimental

4.1. General

Unless otherwise stated, NMR spectra were recorded in deuterated chloroform at 300 MHz (^{1}H NMR) and 282 MHz (^{19}F NMR). ^{13}C NMR spectra were recorded at 75 or 100 MHz in $CDCl_3$. All chemical shifts were reported in ppm relative to TMS and $CFCl_3$ (positive for downfield shifts) as external standards. All coupling constants are reported in hertz. The solvent CH_2Cl_2 was distilled from CaH_2 before use. All starting fluoroalkylsulfinate salts were prepared by using the known procedures [20–25].

4.2. Typical procedure for the preparation of 1a–i

Sodium 2-chloro-1,1,2,2-tetrafluoroethanesulfinate (0.685 g, 3.08 mmol) was placed in a 25 mL round bottom flask equipped with a magnetic stir bar and a nitrogen inlet. Anhydrous dichloromethane (5 mL) and triflic acid (2.70 mL, 30.7 mmol) were added under nitrogen atmosphere. After stirring for 5 min, benzene (0.60 mL, 6.69 mmol) and triflic anhydride (0.60 mL, 3.55 mmol) were introduced. The reaction system was kept stirring at room temperature for 38 h. Then the reaction mixture was poured into ice-water and neutralized by a $NaHCO_3$ solution, extracted with diethyl ether (50 mL), washed with water (3× 20 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography on silica gel using petroleum ether/diethyl ether (10:1) as the eluent. At last, 0.243 g of **1d** (0.93 mmol) was obtained as a light yellow liquid (yield: 30%). ^{1}H NMR: δ 7.81 (d, J = 7.8 Hz, 2H), 7.65 (m, 3H). ^{19}F NMR: δ −66.6 (dd, J = 5.1 Hz, J = 4.5 Hz, 2F), −109.8 (dm, J = 233.0 Hz, 1F), −121.9 (dt, J = 233.0 Hz, J = 5.1 Hz, 1F). ^{13}C NMR: δ 135.3, 133.7, 129.5, 126.7. MS (EI, m/z, %): 260 (M^+, 1.99), 125 (100.00), 97 (26.93), 77 (33.29), 51(20.22). IR (KBr): 3067, 1584, 1477, 1448, 1257, 1178, 1122, 1064, 1017, 902, 803, 749, 688, 485 cm^{-1}. Anal. calcd. for $C_8H_5ClF_4OS$: C, 36.87; H, 1.93; Found: C, 36.71; H, 2.00.

Difluoromethylsulfinylbenzene (**1a**): Colorless liquid. ^{1}H NMR: δ 7.73 (m, 2H), 7.63 (m, 3H), 6.04 (t, J = 55.8 Hz, 1H). ^{19}F NMR: δ −119.1 (dd, J = 55.8 Hz, J = 5.1 Hz, 2F).

Bromodifluoromethylsulfinylbenzene (**1b**): Colorless liquid. ^{1}H NMR: δ 7.81 (d, J = 7.8 Hz, 2H), 7.64 (m, 3H). ^{19}F NMR: δ −52.9 (d, J = 145.3 Hz, 1F), −54.9 (d, J = 145.3 Hz, 1F).

Perfluoroethylsulfinylbenzene (**1c**): Light yellow liquid. ^{1}H NMR: δ 7.81 (d, J = 7.4 Hz, 2H), 7.65 (m, 3H). ^{19}F NMR: δ −79.1 (s, 3F), −115.6 (d, J = 243.3 Hz, 1F), −126.1 (d, J = 243.3 Hz, 1F). ^{13}C NMR: δ 134.7, 133.8, 129.5, 126.6. MS (EI, m/z, %): 244 (M^+, 2.20), 125 (100.00), 97 (32.36), 77 (39.19), 51 (24.67). IR (KBr): 3066, 1584, 1478, 1448, 1333, 1223, 1169, 1127, 1104, 1065, 946, 749, 688, 522, 481 cm^{-1}. Anal. calcd. for $C_8H_5F_5OS$: C, 39.35; H, 2.06; Found: C, 38.92; H, 1.93.

[1,1,2,2-Tetrafluoro-2-(1H-imidazol-1-yl)ethylsulfinyl]benzene (**1e**): Colorless liquid. ^{1}H NMR: δ 7.83 (m, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.63 (m, 3H), 7.20 (s, 2H). ^{19}F NMR: δ −91.4 (dd, J = 227.9 Hz, J = 7.2 Hz, 1F), −92.4 (dd, J = 227.9 Hz, J = 3.1 Hz, 1F), −112.2 (d, J = 240.2 Hz, 1F), −124.9 (dd, J = 240.2 Hz, J = 7.2 Hz, 1F). ^{13}C NMR: δ 134.7, 133.8, 130.7, 129.5, 126.6, 126.5, 116.2. MS (EI, m/z, %): 292 (M^+, 4.24), 125 (100.00), 97 (17.17), 90 (12.58), 77 (22.18), 51 (12.92). IR (KBr): 3125, 3067, 1524, 1483, 1447, 1382, 1299, 1245, 1176, 1127, 1062, 966, 888, 819, 752, 689, 653, 515, 452 cm^{-1}. Anal. calcd. for $C_{11}H_8F_4N_2OS$: C, 45.21; H, 2.76; N, 9.59; Found: C, 45.48; H, 2.89; N, 9.92.

(1,1,2,2-Tetrafluoro-2-phenoxyethylsulfinyl)benzene (**1f**): Colorless liquid. ^{1}H NMR: δ 7.85 (d, J = 7.3 Hz, 2H), 7.64 (m, 3H), 7.41 (t, J = 7.7 Hz, 2H), 7.28 (m, 3H). ^{19}F NMR: δ −80.2 (dd, J = 141.2 Hz, J = 8.2 Hz, 1F), −81.2 (ddd, J = 141.2 Hz, J = 5.1 Hz, J = 4.1 Hz, 1F), −114.5 (dd, J = 232.0 Hz, J = 8.3 Hz, 1F), −125.1 (ddd, J = 232.0 Hz, J = 5.1 Hz, J = 4.1 Hz, 1F). ^{13}C NMR: δ 133.4, 129.7, 129.3, 126.9, 126.8, 126.8, 121.8. MS (EI, m/z, %): 318 (M^+, 17.62), 125 (100.00), 97 (12.55), 77 (31.22), 65 (8.30), 51 (9.96). IR (KBr): 3066, 1591, 1492, 1447, 1326, 1208, 938, 747, 688, 482 cm^{-1}. Anal. calcd. for $C_{14}H_{10}F_4O_2S$: C, 52.83; H, 3.17; Found: C, 53.15; H, 3.29.

(4-Chloro-1,1,2,2,3,3,4,4-octafluorobutylsulfinyl)benzene (**1g**): Light yellow liquid. ^{1}H NMR: δ 7.81 (d, J = 7.8 Hz, 2H), 7.65 (m, 3H). ^{19}F NMR: δ −68.0 (t, J = 13.4 Hz, 2F), −111.2 (d, J = 244.3 Hz, 1F), −118.3–121.1 (m, 4F), −122.5 (dm, J = 244.3 Hz, 1F). ^{13}C NMR: δ 135.0, 133.7, 129.4, 126.7. MS (EI, m/z, %): 360 (M^+, 0.94), 125 (100.00), 97 (26.29), 77 (30.36), 51 (28.46). IR (KBr): 3068, 1584, 1477, 1448, 1309, 1198, 1143, 1104, 1066, 1043, 949, 799, 774, 750, 703, 687, 667, 492, 482, 433 cm^{-1}. Anal. calcd. for $C_{10}H_5ClF_8OS$: C, 33.30; H, 1.40; Found: C, 33.57; H, 1.51.

1-(Difluoromethylsulfinyl)-4-phenylbenzene (**1h**): Colorless solid. ^{1}H NMR: δ 7.81 (m, 4H), 7.62 (m, 2H), 7.47 (m, 3H), 6.09 (t, J = 55.3 Hz, 1H). ^{19}F NMR: δ −119.1 (d, J = 55.3 Hz, 2F). ^{13}C NMR: δ 146.0, 139.3, 135.2, 129.1, 128.5, 128.3, 127.3, 126.0, 121.0 (t, J = 289.9 Hz, CF_2H). MS (EI, m/z, %): 252 (M^+, 4.98), 201 (100.00), 152 (24.72). IR (KBr): 3857, 3747, 3678, 3652, 1592, 1561, 1480, 1451, 1396, 1256, 1124, 1094, 1056, 1045, 1005, 846, 838, 781, 763, 691, 655, 525, 509, 488 cm^{-1}. Anal. calcd. for $C_{13}H_{10}F_2OS$: C, 61.89; H, 4.00; Found: C, 62.15; H, 4.12.

1-(2-Chloro-1,1,2,2-tetrafluoroethylsulfinyl)-4-phenylbenzene (**1i**): Colorless solid. ^{1}H NMR: δ 7.84 (m, 4H), 7.63 (m, 2H), 7.48 (m, 3H). ^{19}F NMR: δ −66.5 (dd, J = 5.1 Hz, 2F), −109.7 (dm, J = 233.1 Hz, 1F), −121.9 (dt, J = 233.1 Hz, J = 5.1 Hz, 1F). ^{13}C NMR: δ 146.8, 139.2, 133.7, 129.1, 128.7, 128.1, 127.4, 127.2. MS (EI, m/z, %): 336 (M^+, 0.75), 201 (100.00), 152 (22.69). IR (KBr): 3063, 3033, 1593, 1561, 1481, 1450, 1399, 1256, 1147, 1119, 1103, 1073, 1053, 1016, 902, 840, 800, 761, 719, 697, 657, 558, 511, 491, 462 cm^{-1}. Anal. calcd. for $C_{14}H_9ClF_4OS$: C, 49.94; H, 2.69; Found: C, 50.44; H, 2.83.

Acknowledgements

We thank the Chinese Academy of Sciences (Hundreds of Talents Program) and the National Natural Science Foundation (20772147, 20972179) for financial support. We thank Dr. Shubin Liu of University of North Carolina for proofreading of the manuscript.

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