Journal of Fluorine Chemistry 145 (2013) 35–40

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis of diazonium (perfluoroalkyl) benzenesulfonylimide zwitterions

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ARTICLE INFO

Article history:
Received 27 July 2012
Received in revised form 16 November 2012
Accepted 20 November 2012
Available online 28 November 2012

Keywords:
Zwitterions
Diazonium salts
Sulfonylimides

ABSTRACT

The synthesis and properties of diazonium (perfluoroalkyl) benzenesulfonylimide (PFSI) zwitterions are described. The general procedures for the diazonium PFSI zwitterions involve three steps: (1) a coupling reaction, (2) a reduction reaction and (3) a diazotization reaction. These novel diazonium PFSI zwitterions represent a new versatile class of remarkably stable diazonium materials with potential for modification of carbon supports for electrodes in proton exchange membrane (PEM) fuel cells.

1. Introduction

Perfluorosulfonic acid (PFSA) polymers, such as Nafion® and Flemion® [1,2], are widely used as the electrolyte membrane for proton exchange membrane (PEM) fuel cells. Among the limitations of PFSA polymers is the relatively weak binding between the fluoropolymer electrolyte and the typical carbon support electrodes. This leads to the gradual loss of electrolyte activity and shortened lifetime of the PEM electrodes [3]. Perfluorinated analogs containing the sulfonimide functional group have been considered as potential alternatives [4].

Bis((perfluoroalkyl)sulfonyl)imides have remarkable acidity because of the strongly electron withdrawing perfluoroalkylsulfonyl group and the delocalization of charge over the O–S–N skeleton in their conjugate bases [5]. The PFSI compounds exhibit better thermal stability in the acid form, chemical and electrochemical inertness, and less susceptibility to dehydration and oxidative degradation reactions than perfluoroalkyl sulfonic acids PFSAs [6]. As a means of improving the electrode–electrolyte binding in PEM electrodes, surface modification of the carbon support using suitable PFSI derivatives has potential [7].

Various diazonium, halonium, sulfonium and alkyl iodides have been used to modify carbon materials [8,9]. Among the different species, diazonium compounds are of particular interest. Carbon surface modification can be initiated by electrochemical reduction or thermal decomposition as shown in Scheme 1. After the facile loss of N_2, the formation of a carbon–carbon covalent bond results in grafting of the aromatic group onto the surface of the carbon [10].

We have briefly described an example of a remarkably stable zwitterionic diazonium PFSI derivative and its successful use in carbon surface modification as shown in Scheme 1 [11]. In this paper we discuss the synthesis and properties of several novel zwitterionic compounds, including multifunctional examples.

2. Results and discussion

2.1. Synthesis

The syntheses of a variety of p-diazonium PFSI zwitterions were achieved via a three-step process: (1) a coupling reaction to prepare a functional 4-nitro(perfluoroalkyl) benzenesulfonylimide, (2) a reduction with sodium polysulfide to give the corresponding 4-amino (perfluoroalkyl) benzenesulfonylimide and (3) a diazotization of the corresponding aminobenzenes. These reactions are summarized in Schemes 2–4 and Tables 1–3.

Two methods were used for the coupling reaction depending on the fluorocarbon group. Method A worked well for simple perfluoroalkyl groups [12]. For the difunctional R_f groups, Method B was the preferred route due to the low yield of the silyl derivative in Method A. The p-nitrobenzenesulfonyl amide was easily prepared from the commercially available sulfonyl chloride. The DIEA promoted SN_2 reaction with the sulfonyl fluoride gave excellent yields [13]. Both Methods A and B require very dry conditions for the coupling reaction to avoid hydrolysis of the silylamide in Method A or the hydrolysis of the sulfonyl fluoride in Method B. The cesium salts **7–12** are surprisingly insoluble in water making their isolation straight forward (see Section 3).

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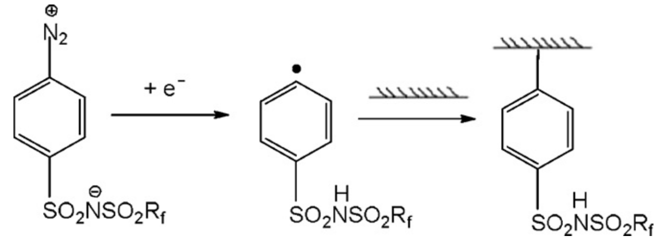
http://dx.doi.org/10.1016/j.jfluchem.2012.11.007



Scheme 1. General mechanism of the grafting reaction of diazonium PFSI zwitterions.

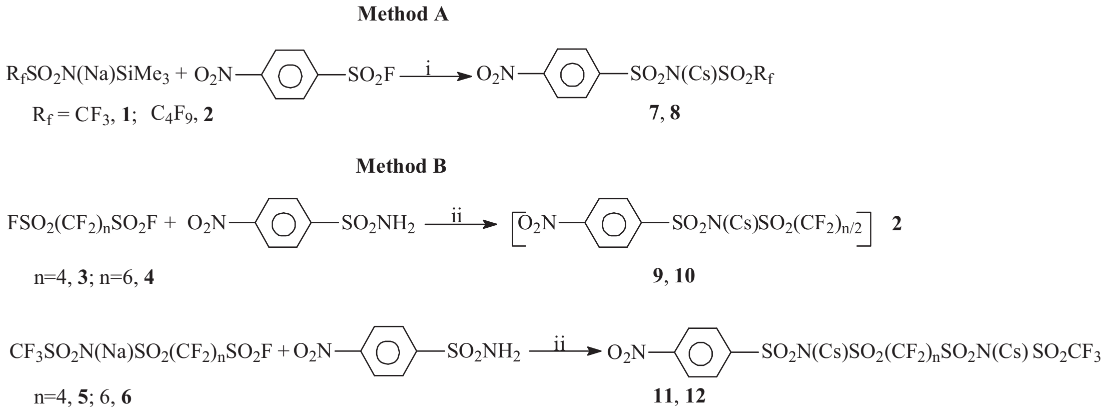
Various reducing agents were tried in order to produce the p-amino PFSIs from the p-nitro PFSI cesium salts. Sodium polysulfide (Na_2S_x, Zinin reduction) was the preferred reducing agent for three reasons: easily prepared, inexpensive commercially available reagents and easily purified products [14]. Other reducing agents, such as $SnCl_2 \cdot H_2O$, also successfully provided the amino product. But the excess tin(II) reducing agent and the tin(IV) byproduct were difficult to separate. The general purification procedure for the latter is to precipitate out the inorganic impurities with base and extract the organic product with ethyl acetate [15]. However, the p-amino PFSI salts could not be dissolved in ethyl acetate because of their polarity. Other polar solvents, such as acetoniltrile, also failed to give the pure 4-amino PFSI compounds by extraction. The Zinin reduction was effective with yields near 90%. A water wash and removal of sulfur with CS_2 gave the PFSIs in high purity.

The final step for these zwitterion syntheses was diazotization. Three diazotization mediums, aqueous, concentrated acids, and organic solvents were utilized [16]. Aromatic amines [13–16] were diazotized and precipitated out with aqueous $H_2SO_4/NaNO_2$ or $HCl/NaNO_2$. However, the multifunctional diazonium PFSI zwitterions **17**–**18**, failed to precipitate out from aqueous solution. This can be explained by their structures with one additional imide group making the product diazonium PFSI zwitterions soluble in water with reaction. Thus for **17**–**18**, isoamyl nitrite and HCl gas in anhydrous ethanol were employed to give the pure diazonium PFSI zwitterions.

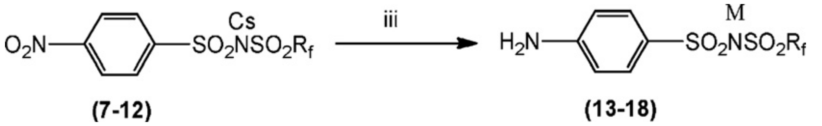
2.2. Structure and properties

Suitable crystals of **19** for single crystal X-ray structure determination were obtained from CH_3CN solution. The structure is shown in Fig. 1. Discrete molecules are visible with interactions between SO_2 oxygen atoms and the diazonium nitrogens. The distances between the diazonium nitrogen and the sulfonimide nitrogen are calculated as 5.3 and 4.6 Å. Attempts to obtain single crystals of **20** were unsuccessful.

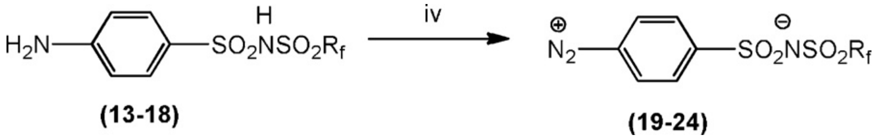
Some properties of the diazonium salts are summarized in Table 4. The onset of thermal decomposition by TGA shows the extraordinary stability of **19** and somewhat less so for **20**–**22**. Compounds **23** and **24** containing the second sulfonamide function are clearly much less stable. All the diazonium salts react with water: **19**–**22** very slowly in air and with liquid H_2O in which they are insoluble. In contrast **23** and **24** are soluble in H_2O with rapid reaction. The solubilities in organic solvents are interesting. The α,ω-bis(PFSI zwitterions) **21** and **22** are much less soluble in CH_3CN than **19**, **20**, **23** and **24** but are reasonably soluble in DMSO. Based on solvent polarity, their solubility should be similar, and the difference is not easily explained. All compounds **19**–**24** can presumably give carbon coatings that are stable above 200 °C as was observed for **19** [11].



Scheme 2. Coupling reaction routes. (i: dry CH_3CN; 36.5% HCl; saturated Cs_2CO_3 solution. ii: dry CH_3CN/DIEA or Et_3N; 36.5% HCl; saturated Cs_2CO_3 solution.)



Scheme 3. Reduction to produce p-amino (perfluoroalkyl) benzenesulfonimide (PFSIs) (iii: Na_2S_x ethanol solution or $SnCl_2$/ethanol).



Scheme 4. Diazotization for diazonium PFSI zwitterions (iv: $HCl/NaNO_2$ or HCl/isoamyl nitrite/dry ethanol).

Table 1
Synthesis of p-nitrobenzene perfluoroalkylsulfonylimide Cs salts.

Compound	Method	Product (yield%)
1	A	7 (82%)
2	A	8 (84%)
3	B[a]	9 (85%)[b]
4	B[a]	10 (84%)[b]
5	B	11 (73%)
6	B	12 (75%)

[a] Ratio of $FSO_2(CF_2)_nSO_2F$ to p-nitrobenzenesulfonyl amide was 1:2.
[b] The purity was around 95% according to ^{19}F NMR spectroscopy. The impurity is the hydrolysis byproduct.

Table 2
Synthesis of p-amino PFSI salts.

Compound	Method[a]	Product[b] (yield%)
7	A	13 (93%)
7	B	13(90%)[c]
8	A	14 (84%)
9	A	15 (85%)[c]
10	A	16 (84%)[c]
11	A	17 (73%)
12	A	18 (75%)

[a] Method A: NaS_x ethanol solution; Method B: $SnCl_2$/ethanol.
[b] Calcd. for M = 100% H.
[c] ^{19}F NMR purity was ~97%.

3. Experimental details

3.1. General considerations

^1H and ^{19}F NMR spectroscopic studies were carried on a Bruker AC 200 (^1H 200.33 MHz and ^{19}F 188.13 MHz) or JEOL ECX-300 (^1H 300.53 MHz and ^{19}F 282.78 MHz). All chemical shifts are quoted in ppm using the high-frequency position convention. NMR spectra were measured using solutions of 1–2 mmol/L (unless otherwise stated) in an appropriate deuterated solvent. ^1H NMR spectra were referenced to external TMS, and ^{19}F chemical shifts were referenced to internal $CFCl_3$. The Infrared spectra were recorded on Perkin-Elmer 1600 and 2000 series FTIR spectrometers. Liquids were run as a film between two KCl plates. Unless indicated otherwise, samples were a minimum of 99.5% pure by ^{19}F NMR spectroscopy. Thermogravimetric analyses were obtained under nitrogen on a Perkin-Elmer TGA7 with heating rates of 20 °C/min. The sample size for the TGA was normally 10–20 mg.

Table 3
Synthesis of p-diazonium PFSI zwitterions.

Comp	Method[a]	Product (yield%)
13	A	19 (86%)
14	A	20 (84%)
15	A	21 (85%)[b]
16	A	22 (84%)[b]
17	B	23 (55%)
18	B	24 (57%)

[a] Method A: $HCl/NaNO_2$; Method B: HCl/isoamyl nitrate/dry ethanol.
[b] The purity was around 95% according to ^{19}F NMR spectroscopy. The impurity was the hydrolysis byproduct.

Table 4
Summary of properties of 4-diazonium PFSI zwitterions $p\text{-}N_2^+PhSO_2N^-SO_2R_f$.

Compound	TGA (°C)	Solubility	Color
19	197.8	CH_3CN	Yellow
20	164.5	CH_3CN	Yellow
21	183.5	$CH_3CN < DMSO$	Yellow
22	153.9	$CH_3CN < DMSO$	Pink
23	80.8	CH_3CN, H_2O	Brown
24	77.1	CH_3CN, H_2O	Brown

The starting materials $CF_3SO_2N(Na)Si(Me)_3$ [6] and the difunctional sulfonylfluorides [17–19] were prepared by published methods. All other starting materials were from commercial sources and were used as received except where noted.

Caution: *Diazonium salts are energetic materials and the dry salts should be treated with due caution. We experienced no incidents in this work, but small sample size is recommended in the absence of further testing.*

3.2. Preparation of p-nitrobenzene sulfonyl fluoride and amide

p-Nitrobenzenesulfonyl chloride (5.00 g, 22.6 mmol) and KF (3.39 g, 67.8 mmol) (1:3) were added into a 50 mL round bottom flask with 30 mL of acetone. The mixture was refluxed at 60 °C for 8 h. A light green solid (3.81 g, 82%) was obtained after removing the solvent and sublimation under high vacuum at 80 °C.

p-Nitrobenzenesulfonylfluoride (10.0 g, 45.2 mmol) was added under N_2 to a 250 mL 3-necked flask. The flask was cooled to −60 °C and 30 mL of ammonia was condensed into the reactor. The mixture was allowed to slowly warm to 22 °C and stand for 8 h. The product was washed 3× with 20 mL of water to remove the NH_4F.

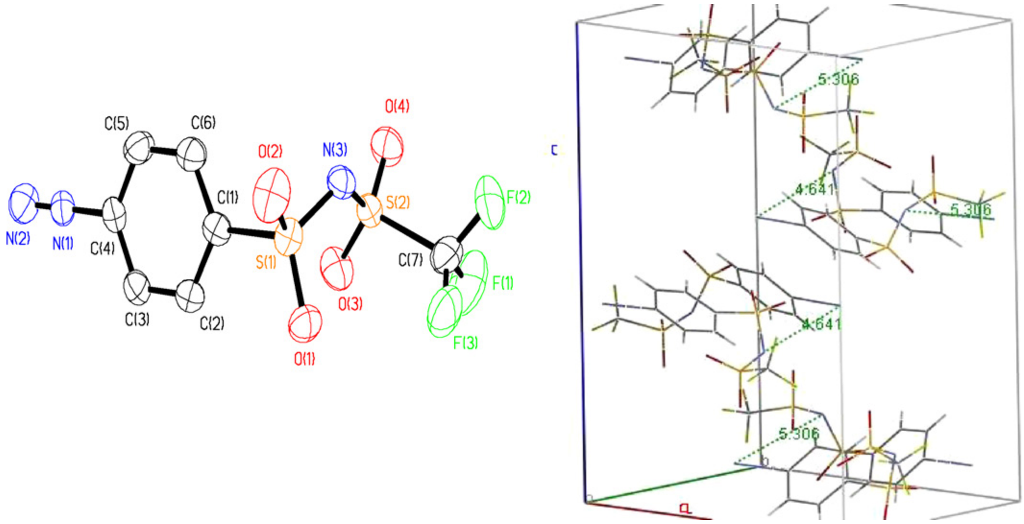


Fig. 1. X-ray structure of $p\text{-}N_2^+PhSO_2N^-SO_2CF_3$ N1–N2 1.085(7) Å; N1–C4 1.406(7) Å.

The solid, yellow product (7.55 g, 81%) was obtained by drying under vacuum for 24 h at 22 °C.

p-NO_2PhSO_2F: ^{19}F NMR (CD_3CN) δ 65.7(s); ^1H NMR (CD_3CN) δ_a 8.46 (2H, d), δ_b 8.27 (2H,d), J_{ab} = 8 Hz. (**Note**: The ^1H represent an aa′bb′ spin system but it appears as a deceptively simple ab system with J/δ near 0.5. The $\delta_{a,b}$ for all compounds are taken as the midpoint of the second order doublets as an approximation as if it is a classic ab spin system. The J_{ab} is assigned as that of a classic ab spin system. No effort was made to analyze the spectra further.)

p-$NO_2PhSO_2NH_2$: ^1H NMR (CD_3CN) δ_a 8.34 (2H, d), δ_b 8.06 (2H,d), J_{ab} = 11 Hz, δ_{NH2} 5.90 (2H,s).

3.3. Synthesis of $CF_3SO_2N(Na)(CF_2)_nSO_2F$ **5–6** (n = 4 or 6)

In a typical procedure $FSO_2(CF_2)_4SO_2F$ (10.98 g, 0.03 mol) was added to $CF_3SO_2N(Na)SiMe_3$ (2.43 g, 0.01 mol) in dry CH_3CN (30 mL) in a 100 mL round bottom flask with the dry N_2 protection. The flask was fitted with a reflux condenser and a $CaSO_4$ drying tube and the mixture was allowed to reflux at 100 °C for 2 days. After cooling to room temperature, excess $FSO_2(CF_2)_4SO_2F$ and the solvent were removed by vacuum distillation. Water (30 mL) was added to the distillate to recover the excess $FSO_2(CF_2)_nSO_2F$. The residue in the reaction flask was dried at 100 °C under high vacuum to afford purified products (**5**, **6**) with isolated yields of 89–92%.

$CF_3{}^ASO_2N(Na)CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ESO_2F^F$ (**5**): ^{19}F NMR (CD_3CN) δ_F 46.7 (1F, s), δ_A −78.9 (3F, s), δ_B −106.6 (2F, t), δ_{C+D} −119.0 (4F, m), δ_D −112.5 (2F, t).

$CF_3{}^ASO_2N(Na)CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^GSO_2F^H$ (**6**): ^{19}F NMR (CD_3CN) δ_H 47.2 (1F, s), δ_A −78.9 (3F, s), δ_G −106.8 (2F, t), δ_B −112.5 (2F,t), δ_{F+C} −119.4 (4F, m), δ_{E+D} −120.3 (4F, m).

3.4. Synthesis of p-nitrobenzenesulfonylperfluoroalkylsulfonyl cesium imides

3.4.1. Compounds **7–8** ($R_f = CF_3$ or C_4F_9)

A typical procedure consisted of adding p-NO_2PhSO_2F (4.1 g, 0.02 mmol) and $CF_3SO_2N(Na)SiMe_3$ (4.86 g, 0.02 mmol) (1:1) in a 100-mL two-necked flask closed by a septum and a PTFE-glass stopcock. Dry CH_3CN (20 mL) and $((CH_3)_2CH)_2NCH_2CH_3$ (DIEA, 4.0 mL) were then injected into the evacuated flask. Dry N_2 was added, and the flask was held at 80 °C for 2 days. ^{19}F NMR showed the reaction was complete. The mixture was treated with 36.5% HCl until acidic (pH < 2). The flask was then placed on a rotary evaporator until a dry crude product was obtained. The solid was dissolved in 15 mL of acetone. Aqueous Cs_2CO_3 (3.26 g in 15 mL) was then added and the precipitated salt was filtered out and washed with H_2O. Drying under high vacuum at 80 °C gave the purified product.

p-$NO_2PhSO_2N(Cs)SO_2CF_3{}^A$ **7** (7.65 g, 82%): ^{19}F NMR (CD_3CN) δ_A −78.16 (3F, s). ^1H NMR (CD_3CN) δ_a 8.26 (2H, d), δ_b 8.05 (2H, d), J_{ab} = 9 Hz;

p-$NO_2PhSO_2N(Cs)SO_2\,CF_2{}^ACF_2{}^BCF_2{}^CCF_3{}^D$ **8** (8.2 g, 81%): ^{19}F NMR (CD_3CN) δ_D −80.32 (3F, t), δ_C −112.47 (2F, m), δ_B −120.46 (2F, m), δ_A −125.26 (2F, t). ^1H NMR (CD_3CN) δ_a 8.26 (2H, d), δ_b 8.05 (2H, d), J_{ab} = 10 Hz.

3.4.2. Compounds **9–10** (n = 2 or 3)

A general procedure consisted of adding dry p-nitrobenzenesulfonyl amide (4.04 g, 0.02 mol) and $FSO_2(C_2F_4)_2SO_2F$ (3.66 g, 0.01 mol) (2:1) to a 50-mL round-bottom flask fitted with an Ace Thread® connection and a glass-Teflon valve. Dry CH_3CN (25 mL) was vacuum transferred into the flask cooled to 196 °C and dry DIEA (4 mL) was then sucked into the flask. ^{19}F NMR spectroscopy showed the reaction was complete after refluxing at 80 °C for 36 h. After acidifying the solution with 36.5% HCl, the solvent was removed under vacuum. The resulting crude product was dissolved in acetone (20 mL) and Cs_2CO_3 (8.15 g, 30 mL) aqueous solution was added. The precipitate was filtered and washed with water, followed by drying under high vacuum at 100 °C for 4 h to afford the product.

(p-$NO_2PhSO_2N(Cs)SO_2CF_2{}^ACF_2{}^B)_2$ **9** (8.5 g, 85%): ^{19}F NMR (CD_3CN) δ_A −112.2 (4F, t), δ_B −119.4 (4F, t). ^1H NMR (CD_3CN) δ_a 8.26 (2H,d), δ_b 8.16 (2H,d) J_{ab} = 9 Hz.

(p-$NO_2PhSO_2N(Cs)SO_2\,CF_2{}^ACF_2{}^BCF_2{}^C)_2$ **10** (8.8 g, 89%): ^{19}F NMR (CD_3CN) δ_A −112.2 (4F, t), δ_B −119.5 (4F, m), δ_C −120.9 (4F, t). ^1H NMR (CD_3CN) δ_a 8.26 (2H, d), δ_b 8.06 (2H, d) J_{ab} = 9 Hz.

3.4.3. Compounds **11–12**

A typical procedure consisted of adding $CF_3SO_2N(Na)(CF_2)_4SO_2F$ (4.84 g, 9.36 mmol) and p-$NO_2PhSO_2NH_2$ (3.80 g, 18.8 mmol) (1:2) into a 50-mL flask as above. Dry CH_3CN (15 mL) and dry DIEA (2 mL) were then sucked into the flask under vacuum. ^{19}F NMR showed the reaction was complete after refluxing at 80 °C for 2 days. After acidifying the solution with 36.5% HCl, the solvent was removed with rotary evaporation. The resulting crude product was dissolved in acetone (20 mL) and recrystallized out with Cs_2CO_3 (7.0 g, 20 mL) aqueous solution. The precipitate was filtered and washed with water and dried under high vacuum at 80 °C for 4 h.

$CF_3{}^ASO_2N(Cs)CF_2{}^{B'}CF_2{}^{C'}CF_2{}^CCF_2{}^BSO_2N(Cs)SO_2PhNO_2$-p **11** (7.65 g, 87%): ^{19}F NMR (CD_3CN) δ_A −78.9 (3F,s), $\delta_{B+B'}$ −112.3 (4F, t), $\delta_{C+C'}$ −119.5 (4F, m); ^1H NMR (CD_3CN) δ_a 8.26(2H,d), δ_b 8.06(2H,d) J_{ab} = 10 Hz.

$CF_3{}^ASO_2N(Cs)CF_2{}^BCF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^GSO_2(Cs)SO_2PhNO_2$-p **12** (8.6 g, 88%): ^{19}F NMR (CD_3CN) δ_A −79.2 (3F, s), δ_G, δ_B −112.2, −112.5 (4F, t), δ_{C+F} −119.5 (4F, m), δ_{D+E} −120.8 (4F, m). ^1H NMR (CD_3CN) δ_a 8.26(2H, d), δ_b 8.06(2H, d) J_{ab} = 10 Hz.

3.5. Synthesis of p-$NH_2PhSO_2NMSO_2R_f$ **13–18**

The Zinin reducing agents were prepared as follows. $Na_2S{\cdot}9H_2O$ (4.80 g, 0.02 mol) was dissolved in water (30 mL) in an ice bath with good stirring. Then H_2S gas produced by adding HCl (36%, 8 mL) dropwise to $Na_2S{\cdot}9H_2O$ (7.2 g, 0.03 mol) was bubbled rapidly into the aqueous solution of $Na_2S{\cdot}9H_2O$. The reagent was refrigerated until used. A typical reaction is described for $R_f = CF_3$.

In a 250 mL two necked flask, p-$NO_2PhSO_2N(Cs)SO_2CF_3$ (7.65 g, 16.42 mmol) was dissolved in ethanol (20 mL). The Zinin reducing agent was then added dropwise into this solution over 1 h at 80 °C and the solution was heated for another 1.5–2.0 h at 80 °C. The mixture was placed on a rotary evaporator at 80 °C and the resulting solid mixture was further dried under high vacuum at 80 °C. The excess S was removed using CS_2 and a Soxhlet extractor. The resulting product was then dried under dynamic vacuum at 22 °C for 8 h and used directly in the next reaction. M represents an undetermined Cs/Na salt and possibly some H.

p-$NH_2{}^cPhSO_2NMSO_2CF_3{}^A$ **13** (4.63 g, 92%): ^{19}F NMR (CD_3CN): δ_A −77.69 (3F,s). ^1H NMR (CD_3CN): δ_a 7.53 (2H,d), δ_b 6.61(2H,d) J_{ab} = 7 Hz, δ_c 4.59 (2H,s);

p-$NH_2{}^cPhSO_2NMSO_2\,CF_2{}^ACF_2{}^BCF_2{}^CCF_3{}^D$ **14** (5.2 g, 88%): ^{19}F NMR (CD_3CN) δ_D −80.33 (3F, t), δ_C −112.49 (2F, m), δ_D −120.48 (2F, m), δ_A −125.20(2F, t). ^1H NMR (CD_3CN) δ_a 7.90 (2H,d), δ_b 7.39 (2H,d) J_{ab} = 6 Hz, δ_c 4.62 (2H,s);

(p-$NH_2{}^cPhSO_2NMSO_2CF_2{}^ACF_2{}^B)_2$ **15** (12.2 g, 75%): ^{19}F NMR (CD_3CN) δ_A −112.4 (4F, t), δ_B −119.4 (4F, t). ^1H NMR (CD_3CN) δ_a 7.93 (2H,d), δ_b 7.52 (2H,d) J_{ab} = 9 Hz, δ_c 3.13(4H,s);

(p-$NH_2{}^cPhSO_2NMSO_2CF_2{}^ACF_2{}^BCF_2{}^C)_2$ **16** (13.1 g, 81%): ^{19}F NMR (CD_3CN): δ_A −112.3 (4F, t), δ_B −119.6 (4F, m), δ_C −121.0 (4F, t). ^1H NMR (CD_3CN) δ_a 7.61 (2H,d), δ_b 6.96 (2H,d) J_{ab} = 9 Hz, δ_c 4.35 (4H,s);

$CF_3{}^ASO_2NMCF_2{}^{B'}CF_2{}^{C'}CF_2{}^CCF_2{}^BSO_2NMSO_2PhNH_2{}^e$-p **17** (3.95 g, 86%): ^{19}F NMR (CD_3CN) δ_A −78.9 (3F,s), $\delta_{B+B'}$ −112.3 (4F, t), $\delta_{c+c'}$ −119.4 (4F, m). ^1H NMR (CD_3CN) δ_a 7.89 (2H,d), δ_b 7.33 (2H,d) J_{ab} = 10 Hz, δ_e 4.59 (2H, s);

$CF_3{}^{A}SO_2N(M)CF_2{}^{B}CF_2{}^{C}CF_2{}^{D}CF_2{}^{E}CF_2{}^{F}CF_2{}^{G}SO_2NMSO_2PhNH_2{}^{c}$-p **18** (4.2 g, 88%): ^{19}F NMR (CD_3CN) δ_A −78.9 (3F,s), δ_{G+B} −112.4 (4F, t), δ_{F+C} −119.5 (4F, m), δ_{D+E} −120.8 (4F, t). ^1H NMR (CD_3CN) δ_a 7.53 (2H, d), δ_b 6.60 (2H, d), J_{ab} = 9 Hz, δ_c 4.56 (2H, s).

3.6. Synthesis of p-$N_2{}^{+}PhSO_2N^{-}SO_2R_f$ ***19–22***

A typical procedure consisted of dissolving p-$NH_2PhSO_2N(M)$-SO_2CF_3 (4.63 g, 15.23 mmol) in hydrochloric acid (36.5%, 10 mL) in a 50-mL round-bottomed flask with good stirring. To the solution was then added the mixture of hydrochloric acid (36.5%, 3 mL) and sodium nitrite (1.06 g, 15.36 mmol for **19** and **20** and 30.72 mmol for **21** and **22**) at 0 °C. After the solution was stirred for 2 h at 22 °C, the solution was poured into a mixture of cracked ice and water. The precipitate was filtered out and dried under dynamic vacuum to give products **19**–**22**.

p-$N_2{}^{+}PhSO_2N^{-}SO_2CF_3{}^{A}$ **19** (4.14 g, 86%): ^{19}F NMR (CD_3CN): A δ_A −78.24. ^1H NMR (CD_3CN) δ_a 8.50 (2H,d), δ_b 8.33 (2H,d), J_{ab} = 9 Hz. IR (cm^{-1}) (KBr pellet) 2287 (m, $-N_2{}^{+}$),3101(s), 1568(s),1410(s),1332(vs),1191(vs),1136(vs),1159(vs),1056(v-s),1091(s), 841(m), 743(m);

Crystals of **19** for X-ray were obtained from CH_3CN. The crystallographic data are given in Table 5.

Intensity data were collected using a Rigaku Mercury CCD detector and an AFC8S diffractometer. Data reduction including the application of Lp and absorption corrections was done using the CrystalClear program [20]. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 using SHELXTL 6.10 [21]. Hydrogen atom positions were calculated from ideal geometry with coordinates riding on the parent atom.

Crystallographic data have been deposited with the Crystallographic Data Center CCDC 607981. Copies may be obtained free of charge on application to the Director CCDC, 12 Union Road, Cambridge CB21EZ, UK (http://www.ccdc.com.ac.uk/conts/retrieving).

p-$N_2{}^{+}PhSO_2N^{-}SO_2$ $CF_2{}^{A}CF_2{}^{B}CF_2{}^{C}CF_3{}^{D}$ **20** (4.4 g, 80%): ^{19}F NMR (CD_3CN) δ_D −80.31 (3F, t), δ_C −112.37 (2F, m), δ_B −120.47 (2F, m), δ_A −125.22 (2F, t). ^1H NMR (CD_3CN): δ_a 8.55 (2H, d), δ_b 8.33 (2H,d) J_{ab} = 9 Hz. IR (cm^{-1}, KBr pellet, nujol): 2287 (s, $-N_2{}^{+}$), 3100(s), 1567(s), 1458(s),1408(s),1333(vs),1313(s), 1300(s), 1232(s), 1194(vs), 1145(vs), 1090(s), 1074(s), 847(m), 817(m);

(p-$N^{+}{}_2PhSO_2N^{-}SO_2$ $CF_2{}^{A}CF_2{}^{B})_2$ **21** (5.96 g, 85%, 95% purity by ^{19}F NMR): ^{19}F NMR (CD_3CN): δ_A −112.1 (4F, t), δ_B −119.4 (4F, t). ^1H NMR (CD_3CN) δ_a 8.65 (2H, d), δ_b 8.28 (2H, d), J_{ab} = 9 Hz. IR (cm^{-1}) (KBr pellet, nujol): 2294 (s, $-N_2{}^{+}$), 3100(s), 1569(s), 1520(s), 1336(vs),1309(s), 1300(s), 1200(vs), 1147(vs), 1093(s), 1078(s), 1053(s), 1611(m), 1569(m), 1520(m), 1409(s), 855(m), 7401(m);

(p-$N^{+}{}_2PhSO_2N^{-}SO_2CF_2{}^{A}CF_2{}^{B}CF_2{}^{C})_2$ **22** (6.3 g, 88%): ^{19}F NMR (CD_3CN): δ_A −112.2 (4F, t), δ_B −119.6 (4F, m), δ_C −121.1 (4F, t). ^1H NMR (CD_3CN) δ_a 8.55 (2H, d), δ_b 8.32 (2H, d) J_{ab} = 9 Hz. IR (cm^{-1}) (KBr pellet, nujol): 2288 (s, $-N_2{}^{+}$), 3100(s), 1569(m), 1458(vs),1465(vs), 1408 (m), 1376(s), 1334 (s), 1306 (s), 1210 (vs), 1150 (vs), 1090 (s), 1077 (s), 840 (m), 7212 (m).

3.6.1. Compounds ***23–24*** (n = 4,6)

A typical procedure consisted of mixing p-$NH_2PhSO_2N(Na)$-$SO_2(CF_2)_4SO_2N(Na)SO_2CF_3$ (2.0 g, 2.89 mmol) with absolute alcohol (4 mL) in a 100 mL two-necked round bottom flask with good stirring. To the solution was then added absolute alcohol (30 mL) saturated with hydrogen chloride gas. Isoamyl nitrite (2 mL) in ether (10 mL) was then added drop wise over 5 min at −5 °C. After stirring for another 20 min, the precipitate was filtered out, washed with cold ether (20 mL) and dried under high vacuum to give pure product. The compound was protected from light by Al foil.

Table 5
Crystallographic data for **19**.

Empirical formula	C7 H4 F3 N3 O4 S2
Formula weight	315.25
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 12.539(3) Å, alpha = 90° b = 9.6700(19) Å, beta = 90° c = 18.927(4) Å, gamma = 90°
Volume	2294.9(8) $Å^3$
Z, Calculated density	8, 1.825 Mg/m^3
Absorption coefficient	0.520 mm^{-1}
F(0 0 0)	1264
Crystal size	0.46 mm × 0.12 mm × 0.07 mm
Theta range for data collection	2.15–25.10°
Limiting indices	$-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-22 \leq l \leq 20$
Reflections collected/unique	18,695/2040 [R(int) = 0.1071]
Completeness to theta = 25.10	99.8%
Absorption correction	REQAB (multi-scan)
Max. and min. transmission	0.9645 and 0.7961
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2040/0/176
Goodness-of-fit on F^2	1.104
Final R indices [$I > 2$sigma(I)]	$R1$ = 0.0684, $wR2$ = 0.1643
R indices (all data)	$R1$ = 0.1032, $wR2$ = 0.1876
Largest diff. peak and hole	0.440 and −0.331 e $Å^{-3}$

$CF_3{}^{A}SO_2N(H){}^{D}SO_2CF_2{}^{B'}CF_2{}^{C'}CF_2{}^{C}CF_2{}^{B}SO_2N^{-}SO_2PhN_2{}^{+}$-p **23** (1.4 g, 76%): ^{19}F NMR (CD_3CN): δ_A −8.9 (3F, s), $\delta_{B+B'}$ −112.3 (4F, m), $\delta_{C+C'}$ −119.5 (4F,m). ^1H NMR (CD_3CN) δ_a 8.55 (2H, d), δ_b 8.32(2H, d) J_{ab} = 9 Hz, δ_D 3.40 (1H, m). IR (cm^{-1}) (KBr pellet, acetone): 2291 (s, $-N_2{}^{+}$), 3104(s), 1706(m), 1569(m), 1411.1(m), 1335(vs), 1196(vs), 1148(vs), 1092(s), 1060(s), 840(m), 787(m)

$CF_3{}^{A}SO_2N(H){}^{H}SO_2CF_2{}^{B}CF_2{}^{C}CF_2{}^{D}CF_2{}^{E}CF_2{}^{F}CF_2{}^{G}SO_2N^{-}SO_2PhN_2{}^{+}$-p **24** (1.7 g, 80%): ^{19}F NMR (CD_3CN): δ_A −78.9 (3F, s), δ_{G+B} −112.3 (4F, t), δ_{F+C} −119.4 (4F, m), δ_{D+E} −120.9 (4F, m). ^1H NMR (CD_3CN) δ_a 8.54 (2H, d), δ_b 8.31 (2H, d) J_{ab} = 9 Hz, δ_H 3.51 (1H, m). IR (cm^{-1}) (KBr pellet, acetone): 2289 (s, $-N_2{}^{+}$),3103 (s), 1709 (m), 1571(m), 1411 (m), 1334 (vs), 1203 (vs), 1148 (vs), 1093 (s), 1068 (s), 841 (m), 784 (m).

Acknowledgements

Financial support of this work by the U.S. National Science Foundation, Grant DMI-0303645, and the U.S. Department of Energy, Contract DE-FG02-05ER15718, is gratefully acknowledged.

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