Journal of Fluorine Chemistry 131 (2010) 867–872

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Reactions of fluoroalkanesulfonyl azides with pyrrole and its derivatives

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 27 April 2010
Accepted 18 May 2010
Available online 25 May 2010

Keywords:
Fluoroalkanesulfonyl azide
Pyrrole
Dipolar cycloaddition
Fluoroalkanesulfonyl amide

ABSTRACT

The reactions of fluoroalkanesulfonyl azides with pyrrole and its derivatives were studied. The reaction proceeded smoothly under mild conditions to give the 3-(fluoroalkanesulfonamido) pyrroles in good yield. The electron donating groups on the pyrrole core accelerated the reaction, while the electron withdrawing groups decelerated it. All the products were fully characterized by spectrum methods, and one of the products was further confirmed by X-ray diffraction analysis. A possible reaction mechanism for these reactions was proposed.

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1. Introduction

Many azides, such as phenyl azide, alkane- or arene-sulfonyl azide and azidoformates, when heated or irradiated, undergo decomposition and react *via* a nitrene intermediate [1]. Due to the 1,3-dipolar property of the azide group, they are also readily reacted with many unsaturated compounds, especially with the electron-rich olefins *via* 1,3-dipolar cycloaddition process [2].

However, it was noticed that the reactions of azides with pyrrole and its derivatives have not been reported up to now. During our systematical study on the chemical transformation of fluoroalkanesulfonyl azides **1**, we found that numerous aza-heterocyclic compounds reacted with **1** smoothly. For instance, the indoles reacted readily with **1** and gave many different products according to the substituent groups of indoles (Scheme 1) [3].

Considering about the structure similarity between pyrrole and indole, recently, we investigated the reactions of fluoroalkanesulfonyl azides **1** with pyrrole and its derivatives **2** in detail. All the reactions proceeded through a [2 + 3] cycloaddition process *via* a 1,2,3-triazole intermediate. It was also found that electronic effect of the substituent of pyrrole on the reaction process was obvious. Herein, we report these results and discuss the reaction mechanism.

2. Results and discussion

The reaction of fluoroalkanesulfonyl azide **1a** with pyrrole **2a** was first investigated. At room temperature, **1a** (2.2 mmol) was added dropwise to a solution of pyrrole **2a** (2.0 mmol) and MeCN (10 mL) in a 25 mL three-necked flask. The reaction mixture turned pale yellow slowly and the nitrogen gas released. After addition, the reaction temperature was increased to 80 °C, the reaction mixture turned blue-black. After stirring for 2 h, the reaction was finished according to TLC analysis. After removing the solvent, the residue was subjected to flash column chromatography using petroleum ether–ethyl acetate = 1:1 as eluant, to give the pure product **3aa** as blue oil in a yield of 86%.

Product **3aa** was fully characterized by spectroscopic and elemental analysis. Its ^{1}H NMR spectrum was composed of five peaks, which are 8.26 (br s), 6.62 (br s), 6.85 (dd), 6.68 (dd) and 6.17 (d) ppm. Two broad singlets could be assigned to two active NHs (8.26 for SO_2NH and 6.62 for pyrrole NH). Comparing with the standard ^{1}H NMR spectrum of pyrrole (2,5-H at 6.62 ppm, 3,4-H at 6.05 ppm), the two peaks at 6.85 and 6.68 ppm should be 2,5-H of the pyrrole core. The remained peak at 6.17 ppm was assigned to 4-H of **3aa**. Thus, the R_fSO_2NH group should be substituted at 3-possition of the pyrrole ring. A typical broad absorption at 3435 cm^{-1} and 3299 cm^{-1} in its FT-IR spectrum also confirmed the existence of R_fSO_2NH group and pyrrole core NH. In addition, the R_f (ICF_2C-$F_2OCF_2CF_2$) group remained unchanged, because the ^{19}F NMR of **3aa** (−65.5, −82.3, −86.0 and −114.7 ppm) was nearly the same as **1a** (−65.1, −81.7, −86.7 and −113.8). ESI-MS showed that the molecular weight of **3aa** was 488. Together with elemental analysis and previous literature works, the structure was determined as 3-(3-oxa-5-iodo-octafluoropentanesulfonamido) pyrrole.

Under the same reaction conditions, other azides **1(b-d)** reacted with pyrrole **2a** smoothly and all gave the 3-(fluoroalkanesulfonylamido) pyrroles in yields of 75–91% (Table 1, Entry 1–4). Product **3da** gave a fine crystal when it was recrystallized in a solution of petroleum ether and ethyl acetate. Its X-ray diffraction analysis further confirmed the 3-subsituted structure (Fig. 1) and

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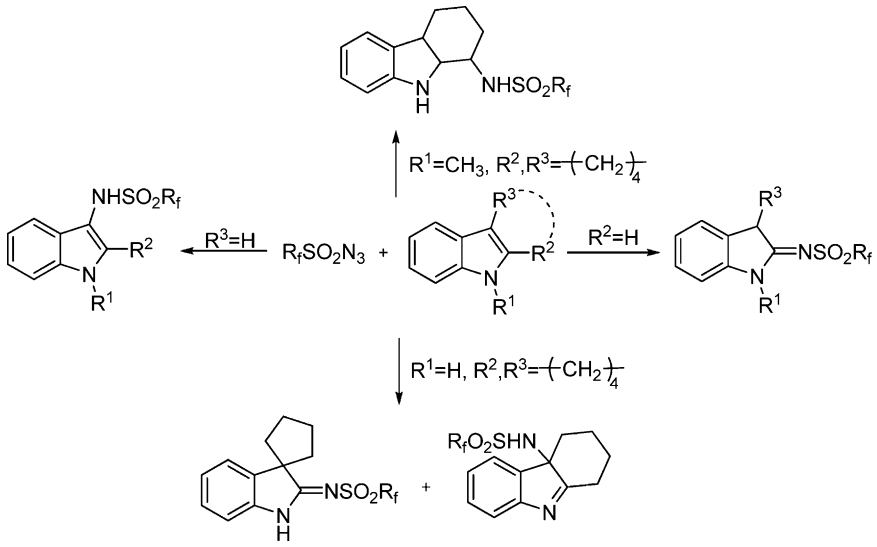
0022-1139/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jfluchem.2010.05.005

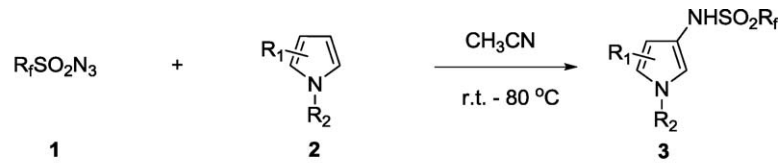


Scheme 1. Reactions of fluoroalkanesulfonyl azides with indoles.

also showed there were strong intermolecular hydrogen bonds between C=O...H–N (d O···H–N 2.047 Å) and SO_2···H–N (d O···H–N 2.471 Å) (Fig. 2).

It was noticed that the reaction of N-methyl pyrrole **2b** with azides was finished within 0.5 h (Table 1, Entry 5–9). In the case of 1,2,5-trimethyl pyrrole **2c**, when the azide was added dropwise to the solution of **2c** in CH_3CN, the nitrogen gas released violently, and the product was formed immediately (Table 1, Entry 9–12). It is clearly that, the electron donating group increased the electron density of the pyrrole cycle, which accelerated the reaction and made the reaction process much easier. In contrast to the methyl substituted pyrroles **2b** and **2c**, N-phenyl pyrrole **2d** reacted with azides very slowly. After refluxing in CH_3CN for 30 h, there was still more than 10% of **2d** remained (Table 1, Entry 13–16). While

Table 1
Results of reactions of fluoroalkanylsulfonyl azides with indole derivatives



R_f= $IC_2F_4OC_2F_4$ **(a)**; $HC_2F_4OC_2F_4$ **(b)**; C_4F_9 **(c)**; *i*-$C_3H_7OCOCF_2$ **(d)**; CH_3OCOCF_2 **(e)**

R_1 = H, R_2 = H **(a)**; R_1 = H, R_2 = CH_3 **(b)**; R_1 = 2, 5-CH_3, R_2 = CH_3 **(c)**; R_1 = H, R_2 = Ph **(d)**; R_1 = H, R_2 = Boc **(e)**; R_1 = 2-$COCH_3$, R_2 = H **(f)**

yield: 75~92 %

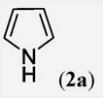
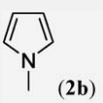
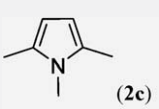
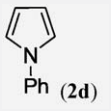
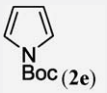
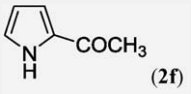
Entry	Azide	Pyrrole	Molar ratio of **1**:**2**	Conditions		Product	Yield (%)[a]
				Time	Temperature (°C)		
1	**1a**	 (**2a**)	1.1:1	2 h	80	**3aa**	86
2	**1b**					**3ba**	90
3	**1c**					**3ca**	91
4	**1d**					**3da**	75
						3ab	89
5	**1a**	 (**2b**)	1.1:1	0.5 h	80		
6	**1b**					**3bb**	92
7	**1c**					**3cb**	90
8	**1d**					**3db**	78
						3ac	81
9	**1a**	 (**2c**)	1.1:1	5 min	25		
10	**1b**					**3bc**	85
11	**1c**					**3cc**	88
12	**1e**					**3ec**	79

Table 1 (*Continued*)

Entry	Azide	Pyrrole	Molar ratio of **1**:**2**	Conditions		Product	Yield (%)[a]
				Time	Temperature (°C)		
13	**1a**	 (**2d**)	1.1:1	30 h	80	**3ad**	76(10)[b]
14	**1b**					**3bd**	83(11)[b]
15	**1c**					**3cd**	85(10)[b]
16	**1e**					**3ed**	82(17)[b]
17	**1c**	 (**2e**)	[1,0]1.1:1	32 h	80	–	–
18	**1c**	 (**2f**)		2 d	80	–	–

[a] Isolated yield based on **2**.
[b] Recover of **2**.

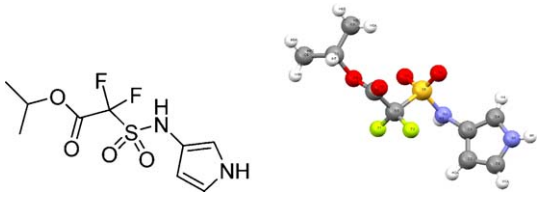


Fig. 1. Molecular structure of **3da**.

2-acetyl pyrrole and N-*t*-butoxycarbonyl pyrrole both have an electron withdrawing group on the pyrrole cycle, they did not react with the azide even refluxing in CH_3CN for 32 h or even 2d (Table 1, Entry 17, 18).

Generally speaking, there are two types of mechanism for the reactions of azide compounds, which are nitrene intermediate and dipolar cycloaddition process. To the best of our knowledge, the former proceeded at high temperature (usually above 110 °C for fluoroalkanesulfonyl azides **1**) and the latter occurred at lower temperature [4]. Thus, the reaction pathway for these reactions is proposed as shown in Scheme 2.

In this reaction, the emission of gas was observed from rt to 80 °C. So the probable pathway is a dipolar cycloaddition followed by a ring-opening process. The [2 + 3] cycloaddition process gave two 1,2,3-triazole intermediates **A** and **B**. Considering about the charge distribution of azide **1** and pyrrole **2**, triazole **A** should be the major intermediate. Due to the strong electron withdrawing property of R_fSO_2NH group, they are unstable and ready to release nitrogen gas to form aziridine intermediate **D**, with subsequent ring-opening and H-shift process gave the final product **3** [5]. On the other hand, when the N–N bond breaking of the triazole intermediate **A**

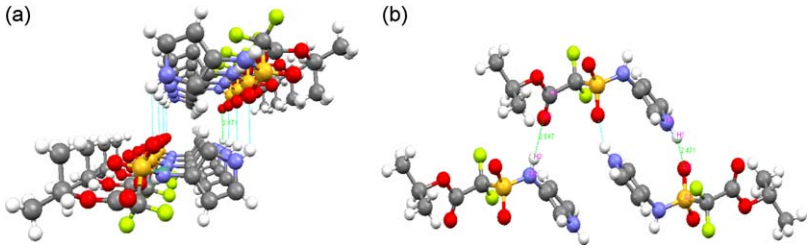
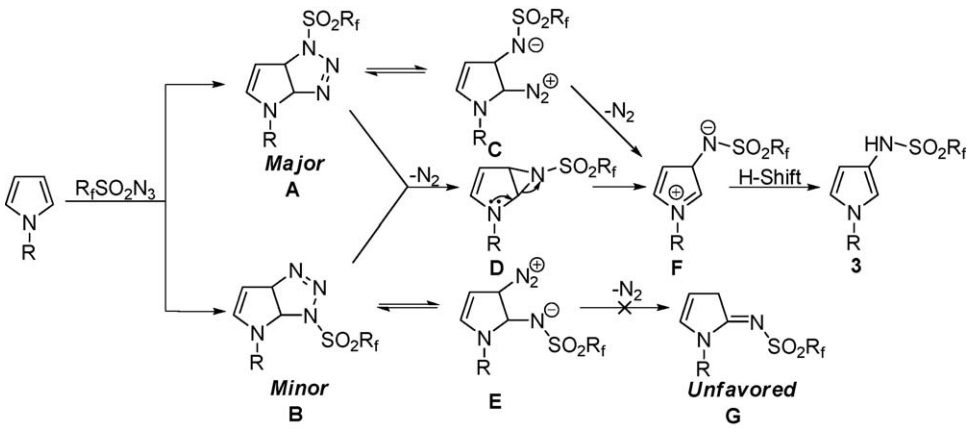


Fig. 2. Packing map of compound **3da**.



Scheme 2. Probable mechanism of the reaction of fluoroalkanesulfonyl azides with pyrrole.

occurred, the zwitterion intermediate **C** was formed, which was also ready to lose N_2 and finally form the product **3**. But the similar zwitterion intermediate **E** did not afford the unfavored amidine product **G**. Thus, compound **3** were obtained exclusively [6].

3. Conclusion

We conducted a detailed investigation on the reactions of fluoroalkanesulfonyl azides with pyrrole and its derivatives and found that the reaction could proceed smoothly under mild conditions and in good yield to give the 3-(fluoroalkanesulfonylamido) pyrroles as the exclusive products. It was found that electron donating groups on the pyrrole core accelerated the reaction, while the electron withdrawing groups decelerated it. The structure of the product was further confirmed by X-ray diffraction analysis. The probable mechanism was proposed as a [2 + 3] dipolar cycloaddition process followed by ring-opening process.

4. Experimental

Melting points are measured on a Temp-Melt apparatus and are uncorrected. ^{1}H (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on a Bruker AM-300 ultra shield, 300 MHz, high performance digital FT-NMR spectrometer with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV) or Electrospray Ionization. Elemental analyses were performed by this Institute. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument. All solvents and reagents were used without further purification unless otherwise stated.

5. General procedure

To a solution of pyrrole **2a** (0.14 mL, 2.0 mmol) and MeCN 10 mL in a 25 mL three-necked flask, **1a** (998 mg, 2.2 mmol) was added dropwise at room temperature. After addition, the mixture was heated to 80 °C for 2 h. TLC analysis showed the reaction was finished. Then the solvent was removed using rotary evaporator under vacuum. The product **3aa** (839 mg, 86%) was obtained by flash column chromatography (using petroleum ether–ethyl acetate = 1:1 as eluant).

5.1. 3-(3-Oxa-5-iodo-octafluoropentanesulfonamido) pyrrole **3aa**

Blue oil. IR (KBr) cm^{-1}: 3435, 3299, 2962, 1591, 1419, 1336, 1295, 1141. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.26 (1H, br s, NH), 6.85 (1H, quart, J = 2.4 Hz), 6.68 (1H, quart, J = 2.7 Hz), 6.62 (1H, br s, NH), 6.17 (1H, d, J = 1.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 128.2, 115.8 (tt, J = 286.8 Hz, 44 Hz), 114.8 (tt, J = 286.8 Hz, 44 Hz), 113.0 (tt, J = 286.8 Hz, 44 Hz), 117.6, 116.7, 115.4, 106.8, 87.8 (tt, J = 317.8 Hz, 44 Hz). (Due to the complicated couplings, the chemical shifts of R_f are not supplied, similarly hereinafter.) ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −65.5 (2F, t, J = 6.5 Hz, ICF_2), −82.3 (2F, t, J = 12.7 Hz, CF_2O), −86.0 (2F, m, OCF_2), −114.7 (2F, s, CF_2S). MS (ESI) m/z: 489.0 ([M + H]$^+$). HRMS (EI) m/z calcd. for $C_8H_5F_8IN_2O_3S$: 487.8938; Found: 487.8929. Anal. Calcd for $C_8H_5F_8IN_2O_3S$: C, 19.69; H, 1.03; N, 5.74%. Found: C, 19.98; H, 0.92; N, 5.49%.

5.2. 3-(3-Oxa-octafluoropentanesulfonamido) pyrrole **3ba**

Blue oil. IR (KBr) cm^{-1}: 3438, 3299, 1560, 1419, 1330, 1284, 1144. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (1H, br s, NH), 6.84 (1H, d, J = 2.4 Hz), 6.68 (1H, quart, J = 3.0 Hz), 6.56 (1H, br s, NH), 6.16 (1H, d, J = 1.5 Hz), 5.80 (1H, tt, J = 3.0, 51.2 Hz, HCF_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.4 (2F, t, J = 12.4 Hz, CF_2O), −88.4 (2F, m, OCF_2), −114.2 (2F, s, CF_2S), −137.3 (2F, td, J = 4.2, 52.5 Hz, CF_2H). MS (EI) m/z: 362 (M$^+$, 8), 81 (M-R_fSO_2, 100). HRMS (EI) m/z calcd. for $C_8H_6F_8N_2O_3S$: 361.9971; Found: 361.9982. Anal. Calcd for $C_8H_6F_8N_2O_3S$: C, 26.53; H, 1.67; N, 7.73%. Found: C, 26.74; H, 1.75; N, 7.99%.

5.3. 3-(Perfluorobutanesulfonamido) pyrrole **3ca**

Blue solid. Mp = 107–109 °C. IR (KBr) cm^{-1}: 3410, 3265, 1556, 1417, 1364, 1237, 1185, 1141. ^{1}H NMR (acetone-d_6, 300 MHz): δ = 6.90 (1H, d, J = 1.8 Hz), 6.75 (1H, d, J = 1.8 Hz), 6.11 (1H, s). ^{19}F NMR (acetone-d_6, 282 MHz): δ = −82.1 (3F, t, J = 9.6 Hz, CF_3), −112.4 (2F, t, J = 14.2 Hz, CF_2S), −122.3 (2F, s, CF_2), −127.1 (2F, dt, J = 7.1, 13.8 Hz, CF_2). MS (ESI) m/z: 365.1 ([M + H]$^+$). HRMS (ESI) m/z 364.9991 ([M + H]$^+$, $C_8H_6F_9N_2O_2S$ required 365.0001). Anal. Calcd for $C_8H_5F_9N_2O_2S$: C, 26.38; H, 1.38; N, 7.69%. Found: C, 26.67; H, 1.19; N, 7.82%.

5.4. 3-(Isopropoxycarbonyldifluoromethenesulfonamido) pyrrole **3da**

Blue solid. Mp = 89–91 °C. IR (KBr) cm^{-1}: 3421, 3297, 1757, 1560, 1429, 1398, 1173, 1093. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.21 (1H, br s, NH), 6.87 (1H, s), 6.68 (1H, quart, J = 2.7 Hz), 6.44 (1H, br s, NH), 6.20 (1H, s), 5.22 (1H, quart, J = 6.0 Hz, OCH), 1.36 (6H, d, J = 6.0 Hz, $2CH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −106.8 (s, CF_2S). MS (ESI) m/z: 283.1 ([M + H]$^+$). HRMS (EI) m/z calcd. for $C_9H_{12}F_2N_2O_4S$: 282.0486; Found: 282.0484.

Crystal data for $C_9H_{12}F_2N_2O_4S$: MW = 282.27, triclinic, space group P−1, a = 7.1451 (6), b = 8.6746(7), c = 11.0128(10) Å, α = 70.000(8), (= 71.190(8), γ = 87.162(7), V = 605.74(9) Å^3, Z = 2, Dc = 1.548 mg/m^3, F (0 0 0) = 292, crystal dimension 0.26 mm × 0.22 mm × 0.17 mm, radiation, Mo Ka (λ = 0.711 Å), $5.30 \leq 2(\leq 50.48$, intensity data were collected at 293 K with a Bruker axs D8 diffractometer, and employing (/2(scanning technique, in the range of $-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$; The structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 2158 observed reflections with R (int) = 0.0344 by a full-matrix least-squares technique converged to R = 0.0629 and Rw = 0.0757.

CCDC reference number is 771792.

5.5. N-Methyl-3-(3-oxa-5-iodo-octafluoropentanesulfonamido) pyrrole **3ab**

Orange oil. IR (KBr) cm^{-1}: 3297, 2953, 1515, 1421, 1336, 1294, 1092. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.62 (1H, s), 6.41 (1H, t, J = 2.4 Hz), 6.38 (1H, br s, NH), 6.00 (1H, s), 3.55 (3H, s, NCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −65.3 (2F, t, J = 5.6 Hz, ICF_2), −82.2 (2F, t, J = 13.3 Hz, CF_2O), −85.9 (2F, m, OCF_2), −114.6 (2F, s, CF_2S). MS (ESI) m/z: 502.8 ([M + H]$^+$), 524.8 ([M + Na]$^+$). Anal. Calcd for $C_9H_7F_8I$-N_2O_3S: C, 21.53; H, 1.41; N, 5.58%. Found: C, 21.90; H, 1.74; N, 5.61%.

5.6. N-Methyl-3-(3-oxa-octafluoropentanesulfonamido) pyrrole **3bb**

Yellow oil. IR (KBr) cm^{-1}: 3299, 2962, 1516, 1421, 1329, 1285, 1136, 1010. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.61 (1H, s), 6.41 (1H, s), 6.38 (1H, br s, NH), 5.99 (1H, s), 5.73 (1H, tt, J = 3.0, 52.8 Hz, HCF_2), 3.55 (3H, s, NCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.9 (2F, t,

J = 10.7 Hz, CF_2O), −88.9 (2F, m, OCF_2), −114.7 (2F, s, CF_2S), −137.8 (2F, td, J = 5.6, 53.6 Hz, CF_2H). MS (ESI) m/z: 377.0 ($[M + H]^+$), 399.0 ($[M + Na]^+$).Anal. Calcd for $C_9H_8F_8N_2O_3S$: C, 28.73; H, 2.14; N, 7.45%. Found: C, 29.04; H, 2.46; N, 7.43%.

5.7. N-Methyl-3-(perfluorobutanesulfonamido) pyrrole **3cb**

White solid. Mp = 42–44 °C. IR (KBr) cm^{-1}: 3301, 2955, 1516, 1422, 1352, 1189, 1141, 1035. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.63 (1H, s), 6.42 (1H, t, J = 2.7 Hz), 6.40 (1H, br s, NH), 6.00 (1H, s), 3.56 (3H, s, NCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.3 (3F, t, J = 10.2 Hz, CF_3), −111.0 (2F, t, J = 13.5 Hz, CF_2S), −121.5 (2F, m, CF_2), 126.4 (2F dt, J = 6.2, 13.0 Hz, CF_2). MS (ESI) m/z: 379.0 ($[M + H]^+$), 401.0 ($[M + Na]^+$) Anal. Calcd for $C_9H_7F_9N_2O_2S$: C, 28.58; H, 1.87; N, 7.41%. Found: C, 28.95; H, 2.18; N, 7.26%.

5.8. N-Methyl-3-(isopropoxycarbonyldifluoromethenesulfonamido) pyrrole **3db**

Orange solid. Mp = 55–57 °C. IR (KBr) cm^{-1}: 3296, 2988, 2942, 1766, 1515, 1379, 1304, 1189, 1097. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.69 (1H, s), 6.47 (1H, s), 6.34 (1H, br s, NH), 6.08 (1H, s), 5.22 (1H, quint, J = 6.3 Hz, OCH), 3.60 (3H, s, NCH_3), 1.35 (6H, d, J = 6.0 Hz, $2CH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −106.7 (2F, s, CF_2S). MS (ESI) m/z: 297.1 ($[M + H]^+$), 319.0 ($[M + Na]^+$). Anal. Calcd for $C_{10}H_{14}F_2N_2O_4S$: C, 40.54; H, 4.76; N, 9.45%. Found: C, 40.61; H, 4.72; N, 9.22%.

5.9. 1,2,5-Trimethyl-3-(3-oxa-5-iodo-octafluoropentanesulfonamido) pyrrole **3ac**

Red solid. Mp = 95–97 °C. IR (KBr) cm^{-1}: 3269, 1512, 1413, 1332, 1292, 1175, 1151, 1092. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.18 (1H, br s, NH), 5.78 (1H, s), 3.35 (3H, s, NCH_3), 2.17 (3H, s, CH_3), 2.15 (3H, s, CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −65.3 (2F, t, J = 5.6 Hz, ICF_2), −82.1 (2F, t, J = 13.3 Hz, CF_2O), −86.0 (2F, m, OCF_2), −115.1 (2F, s, CF_2S). MS (ESI) m/z: 531.0 ($[M + H]^+$). Anal. Calcd for $C_{11}H_{11}F_8IN_2O_3S$: C, 24.92; H, 2.09; N, 5.28%. Found: C, 25.18; H, 2.42; N, 5.44%.

5.10. 1,2,5-Trimethyl-3-(3-oxa-octafluoropentanesulfonamido) pyrrole **3bc**

Red oil. IR (KBr) cm^{-1}: 3226, 2928, 1614, 1525, 1412, 1333, 1219. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.25 (1H, br s, NH), 5.82 (1H, tt, J = 3.0, 51.2 Hz, HCF_2), 5.77 (1H, s), 3.35 (3H, s, NCH_3), 2.16 (3H, s, CH_3), 2.14 (3H, s, CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.8 (2F, t, J = 13.4 Hz, CF_2O), −89.0 (2F, m, OCF_2), −115.3 (2F, s, CF_2S), −137.8 (2F, td, J = 5.1, 51.0 Hz, CF_2H). MS (ESI) m/z: 405.0 ($[M + H]^+$). Anal. Calcd for $C_{11}H_{12}F_8N_2O_3S$: C, 32.68; H, 2.99; N, 6.93%. Found: C, 32.70; H, 3.02; N, 7.20%.

5.11. 1,2,5-Trimethyl-3-(perfluorobutanesulfonamido) pyrrole **3cc**

Red solid. Mp = 53–55 °C. IR (KBr) cm^{-1}: 3251, 1520, 1335, 1136, 1030, 1009. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.25 (1H, br s, NH), 5.77 (1H, s), 3.35 (3H, s, NCH_3), 2.17 (3H, s, $ArCH_3$), 2.15 (3H, s, $ArCH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.1 (3F, t, J = 9.6 Hz, CF_3), −115.5 (2F, t, J = 13.3 Hz, CF_2S), −121.4 (2F, m, CF_2), −126.4 (2F, tt, J = 5.6, 14.4 Hz, CF_2). MS (ESI) m/z: 407.0 ($[M + H]^+$). Anal. Calcd for $C_{11}H_{11}F_9N_2O_2S$: C, 32.52; H, 2.73; N, 6.90%. Found: C, 32.49; H, 2.98; N, 7.11%.

5.12. 1,2,5-Trimethyl-3-(methoxycarbonyldifluoromethenesulfonamido) pyrrole **3ec**

Red solid, Mp = 91–93 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.12 (1H, br s, NH), 5.81 (1H, br s), 3.97 (3H, s, OCH_3), 3.35 (3H, s, NCH_3), 2.17 (3H, s, CH_3), 2.14 (3H, s, CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −107.0 (2F, s, CF_2S). MS (ESI) m/z: 297.0 ($[M + H]^+$), 319.0 ($[M + Na]^+$). Anal. Calcd for $C_{10}H_{14}F_2N_2O_4S$: C, 40.54; H, 4.76; N, 9.45%. Found: C, 40.41; H, 4.78; N, 9.11%.

5.13. N-Phenyl-3-(3-oxa-5-iodo-octafluoropentanesulfonamido) pyrrole **3ad**

Red solid. Mp = 74–76 °C. IR (KBr) cm^{-1}: 3275, 1600, 1519, 1451, 1399, 1330, 1291, 1121. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41–7.36 (2H, m), 7.30 − 7.21 (3H, m), 7.08 (1H, s), 6.90 (1H, t, J = 2.7 Hz), 6.41 (1H, br s, NH), 6.22 (1H, t, J = 2.7 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −65.4 (2F, t, J = 5.9 Hz, ICF_2), −82.1 (2F, t, J = 12.7 Hz, CF_2O), −86.0 (2F, m, OCF_2), −114.5 (2F, s, CF_2S). MS (ESI) m/z: 565.0 ($[M + H]^+$), 587.0 ($[M + Na]^+$). Anal. Calcd for $C_{14}H_9F_8IN_2O_3S$: C, 29.80; H, 1.61; N, 4.97%. Found: C, 29.94; H, 1.88; N, 5.04%.

5.14. N-Phenyl-3-(3-oxa-octafluoropentanesulfonamido) pyrrole **3bd**

Red oil. IR (KBr) cm^{-1}: 3307, 1703, 1601, 1513, 1426, 1109, 1008. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46–7.41 (2H, m), 7.35–7.25 (3H, m), 7.13 (1H, s), 6.95 (1H, t, J = 3.0 Hz), 6.57 (1H, br s, NH), 6.27 (1H, t, J = 3.0 Hz), 5.83 (1H, tt, J = 3.0, 52.5 Hz, HCF_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.9 (2F, t, J = 12.0 Hz, CF_2O), −88.8 (2F, m, OCF_2), −114.6 (2F, s, CF_2S), −137.7 (2F, td, J = 4.9, 50.8 Hz, CF_2H). MS (ESI) m/z: 439.0 ($[M + H]^+$). Anal. Calcd for $C_{14}H_{10}F_8N_2O_3S$: C, 38.36; H, 2.30; N, 6.39%. Found: C, 38.60; H, 2.38; N, 6.50%.

5.15. N-Phenyl-3-(perfluorobutanesulfonamido) pyrrole **3cd**

Red solid. Mp = 59–61 °C. IR (KBr) cm^{-1}: 3304, 2927, 1705, 1601, 1513, 1402, 1351, 1240, 1140, 1034. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.41–7.36 (2H, m), 7.31–7.21 (3H, m), 7.09 (1H, s), 6.90 (1H, t, J = 2.4 Hz), 6.47 (1H, br s, NH), 6.22 (1H, t, J = 2.4 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −81.1(3F, t, J = 9.3 Hz, CF_3), −110.9 (2F, t, J = 13.0 Hz, CF_2S), −121.4 (2F, s, CF_2), −126.4 (2F, dt, J = 4.8, 13.9 Hz, CF_2). MS (ESI) m/z: 441.0 ($[M + H]^+$), 463.0 ($[M + Na]^+$). Anal. Calcd for $C_{14}H_9F_9N_2O_2S$: C, 38.19; H, 2.06; N, 6.36%. Found: C, 38.51; H, 2.40; N, 6.36%.

5.16. N-Phenyl-3-(methoxycarbonyldifluoromethenesulfonamido) pyrrole **3ed**

Red solid. Mp = 78–80 °C. IR (KBr) cm^{-1}: 3286, 1766, 1598, 1509, 1440, 1318, 1134. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.46–7.40 (2H, m), 7.35 − 7.28 (3H, m), 7.15 (1H, s), 6.95 (1H, quart, J = 2.7 Hz), 6.40 (1H, br s, NH), 6.29 (1H, t, J = 2.7 Hz), 3.96 (3H, s, OCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ = −106.5 (2F, s, CF_2S). MS (ESI) m/z: 331.0($[M + H]^+$), 353.0 ($[M + Na]^+$). Anal. Calcd for $C_{13}H_{12}F_2N_2O_4S$: C, 47.27; H, 3.66; N, 8.48%. Found: C, 47.28; H, 3.80; N, 8.41%.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (NNSFC) (No. 20972178). We express our gratitude to Professor Yuepeng Cai from South China Normal University for his help on the single crystal X-ray diffraction analysis.

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