

Novel lithium and sodium salts of sulfonamides and bis(sulfonyl)imides: synthesis and electrical conductivity

Vincent Morizur,^a Sandra Olivero,^a Jean Roger Desmurs,^b Philippe Knauth^c and Elisabet Duñach*^a

Electronic Supplementary Information (ESI) available: [procedure and analysis for the preparation of compounds 2a-2b, 4a-4d, 5a-5d, 6a-6d, 9a-9b, 9e-9f and 10a-10f].

Experimental

Preparation of benzenesulfonyl chloride 2a-2b

In a two-necked 25 mL flask fitted with a condenser, the aromatic compound **1** (nitrobenzene or fluorobenzene) (81 mmol) was added, followed by addition of chlorosulfonic acid (106 mmol) *via* a syringe. The mixture was heated at 150 ° C for 2 h 30. The solution was cooled to room temperature and thionyl chloride was added (1.42 equiv.) and the mixture was then heated at 150 ° C for 3 h. The solution was cooled to room temperature and quenched with 20 mL of water. The aqueous phase was extracted with 3 × 20 mL of ethyl acetate. The combined organic phases were dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel using a mixture of dichloromethane / cyclohexane (50/50) as the eluent.

2a: 3-nitrobenzenesulfonyl chloride

¹H NMR (200 MHz, CDCl₃) δ 8.82 (t, *J* = 2.0 Hz, 1H), 8.55 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.32 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H).

¹³C NMR (50 MHz, CDCl₃) δ 148.33 (s), 145.50 (s), 132.28 (s), 131.34 (s), 129.54 (s), 122.42 (s).

2b: 4-fluorobenzenesulfonyl chloride

¹H NMR (200 MHz, DMSO-D₆) δ 7.73 – 7.46 (m, 1H), 7.22 – 7.02 (m, 1H).

¹³C NMR (50 MHz, DMSO-D₆) δ 144.09 (s), 144.03 (s), 127.89 (s), 127.72 (s), 114.69 (s), 114.26 (s).

Preparation of sulfonamide 4a-4d

In a 50 mL flask, the sulfonyl chloride **2** (2.3 mmol), and the amine **3** (4.8 mmol) were added to 20 mL acetonitrile. The solution was stirred at room temperature for 2 h, the mixture was filtered off and the filtrate was evaporated. The residue was purified by trituration in diethyl ether (3 × 20 mL) and dried under vacuum overnight.

4a: *N*-(3-(trifluoromethyl)phenyl) 4-fluoro-benzenesulfonamide

¹H NMR (200 MHz, DMSO-D₆) δ 10.83 (s, 1H), 7.98 – 7.75 (m, 2H), 7.55 – 7.34 (m, 6H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -61.59 (s, 3F), -105.38 (tt, *J* = 8.8, 5.1 Hz, 1F).

¹³C NMR (50 MHz, DMSO-D₆) δ 166.92 (s), 161.91 (s), 138.36 (s), 135.27 (s, *J* = 3.1 Hz), 135.21 (s), 130.58 (s), 129.81 (s), 129.61 (s), 123.42 (s), 120.56 (d, *J* = 3.8 Hz), 116.84 (s), 116.38 (s), 115.80 (d, *J* = 4.0 Hz).

4b: *N*-(3-(trifluoromethyl)phenyl) 3-nitro-benzenesulfonamide

¹H NMR (200 MHz, DMSO-D₆) δ 11.07 (s, 1H), 8.62 – 8.43 (m, 2H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.66 – 7.31 (m, 4H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -61.57 (s, 3F).

¹³C NMR (50 MHz, DMSO-D₆) δ 147.86 (s), 140.36 (s), 137.78 (s), 132.46 (s), 131.51 (s), 130.83 (s), 130.26 (s), 129.63 (s), 127.83 (s), 123.99 (s), 121.29 (d, *J* = 8.4 Hz), 121.04 (s), 116.41 (s).

4c: *N*-(4-fluorophenyl) 4-fluoro-benzenesulfonamide

¹H NMR (200 MHz, DMSO-D₆) δ 10.27 (s, 1H), 7.73 (dd, *J* = 19.9, 11.6 Hz, 2H), 7.40 (t, *J* = 8.8 Hz, 2H), 7.22 – 6.89 (m, 4H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -105.96 (tt, *J* = 8.8, 5.2 Hz, 1F), -118.06 (tt, *J* = 7.7, 5.9 Hz, 1F).

¹³C NMR (50 MHz, DMSO-D₆) δ 135.40 (s), 133.59 (s), 132.78 (s), 129.76 (s), 129.57 (s), 123.18 (s), 123.01 (s), 116.64 (s), 116.19 (s), 116.13 (s), 115.68 (s).

4d: *N*-(3,5-difluorophenyl)-4-fluorobenzenesulfonamide

¹H NMR (200 MHz, DMSO-D₆) δ 10.96 (s, 1H), 7.91 (dd, *J* = 8.9, 5.1 Hz, 2H), 7.45 (t, *J* = 8.8 Hz, 2H), 6.93 (tt, *J* = 9.4, 2.2 Hz, 1H), 6.85 – 6.63 (m, 2H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -104.91 – -105.20 (m, 1F), -108.09 – -108.46 (m, 2F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 140.34 (s), 135.12 (s, $J = 3.0$ Hz), 135.06 (s), 129.89 (s), 129.70 (s), 116.99 (s), 116.53 (s), 102.37 (s), 101.80 (s), 99.20 (s).

Preparation of Li^+ et Na^+ sulfonamide salts **5a-5d** and **6a-6d**

In a 25 mL flask under nitrogen, the sulfonamide **4** (1 mmol) was dissolved in 15 mL of THF. Lithium or sodium metal (1.1 mmol) was added to the solution and after 18 h at room temperature the mixture was filtered off. The residue obtained was triturated with 2×10 mL of acetonitrile and then dried under vacuum overnight.

5a: *N*-(3-(trifluoromethyl)phenyl) 4-fluoro-benzenesulfonamide lithium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.77 – 7.65 (m, 2H), 7.16 (t, $J = 9.0$ Hz, 2H), 7.08 – 7.00 (m, 2H), 6.97 – 6.89 (m, 1H), 6.69 (d, $J = 7.2$ Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -61.05 (s, 3F), -112.43 (tt, $J = 9.1$, 5.6 Hz, 1F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 151.47 (s), 143.71 (s), 128.57 (s), 128.52 (s), 128.34 (s), 123.89 (s), 114.88 (s), 114.45 (s).

5b: *N*-(3-(trifluoromethyl)phenyl) 3-nitro-benzenesulfonamide lithium salt

^1H NMR (200 MHz, DMSO- D_6) δ 8.46 – 8.37 (m, 1H), 8.20 (ddd, $J = 8.2$, 2.3, 1.0 Hz, 1H), 8.13 – 8.03 (m, 1H), 7.73 – 7.61 (m, 1H), 7.17 – 7.05 (m, 2H), 6.98 (d, $J = 8.4$ Hz, 1H), 6.76 (d, $J = 7.5$ Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -61.13 (s, 3F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 156.50 (s), 150.78 (s), 149.29 (s), 147.28 (s), 132.14 (s), 129.95 (s), 128.81 (s), 124.24 (s), 123.90 (s), 120.34 (s), 116.14 (s), 112.29 (s).

5c: *N*-(4-fluorophenyl) 4-fluoro-benzenesulfonamide lithium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.72 – 7.59 (m, 1H), 7.12 (t, $J = 9.0$ Hz, 1H), 6.68 (d, $J = 7.1$ Hz, 2H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -113.15 (tt, $J = 9.3$, 5.7 Hz, 1F), -129.22 – -129.41 (m, 1F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 128.54 (s), 128.37 (s), 121.06 (s), 120.89 (s), 114.70 (s), 114.24 (s), 113.87 (s).

5d: *N*-(3,5-difluorophenyl)-4-fluorobenzenesulfonamide lithium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.76 – 7.63 (m, 2H), 7.18 (t, $J = 9.0$ Hz, 2H), 6.39 – 6.23 (m, 2H), 6.09 (tt, $J = 9.5$, 2.4 Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -112.08 (tt, $J = 9.1$, 5.6 Hz, 1F), -113.01 – -113.50 (m, 2F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 128.55 (s), 128.31 (s), 115.06 (s), 114.58 (s), 102.33 (s), 101.78 (s).

6a: *N*-(3-(trifluoromethyl)phenyl) 4-fluoro-benzenesulfonamide sodium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.72 (dd, $J = 8.7$, 5.6 Hz, 2H), 7.17 (t, $J = 8.9$ Hz, 2H), 7.09 – 7.00 (m, 2H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.70 (d, $J = 7.2$ Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -61.06 (s, 3F), -112.18 – -112.43 (m, 1F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 151.33 (s), 143.59 (s), 128.58 (s), 128.40 (s), 123.82 (s), 114.92 (s), 114.49 (s).

6b: *N*-(3-(trifluoromethyl)phenyl) 3-nitro-benzenesulfonamide sodium salt

^1H NMR (200 MHz, DMSO- D_6) δ 8.43 (d, $J = 1.8$ Hz, 1H), 8.22 (ddd, $J = 8.1$, 2.3, 1.0 Hz, 1H), 8.11 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.69 (t, $J = 7.9$ Hz, 1H), 7.22 – 6.95 (m, 3H), 6.79 (d, $J = 7.3$ Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -61.15 (s)

^{13}C NMR (50 MHz, DMSO- D_6) δ 150.20 (s), 148.78 (s), 147.30 (s), 132.19 (s), 130.01 (s), 128.89 (s), 124.11 (s), 120.45 (s), 116.24 (s), 112.80 (s).

6c: *N*-(4-fluorophenyl) 4-fluoro-benzenesulfonamide sodium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.67 (dd, $J = 8.7$, 5.7 Hz, 1H), 7.13 (t, $J = 9.0$ Hz, 1H), 6.69 (d, $J = 7.0$ Hz, 2H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -112.94 – -113.13 (m, 1F), -129.06 – -129.31 (m, 1F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 128.58 (s), 128.36 (s), 121.06 (s), 120.89 (s), 114.73 (s), 114.25 (s), 113.81 (s).

6d: *N*-(3,5-difluorophenyl)-4-fluorobenzenesulfonamide sodium salt

^1H NMR (200 MHz, DMSO- D_6) δ 7.71 (dd, $J = 8.8$, 5.6 Hz, 2H), 7.18 (t, $J = 8.9$ Hz, 2H), 6.32 (dd, $J = 11.8$, 2.3 Hz, 2H), 6.09 (tt, $J = 9.5$, 2.4 Hz, 1H).

^{19}F NMR (188 MHz, DMSO- D_6) δ -111.86 – -112.17 (m, 1F), -113.13 – -113.33 (m, 1F).

^{13}C NMR (50 MHz, DMSO- D_6) δ 128.60 (s), 128.36 (s), 115.02 (s), 114.57 (s), 102.30 (s), 101.80 (s).

Preparation of Li^+ and Na^+ bis(sulfonyl)imide salts **9a-9b** ; **9e-9f** and **10a-10f**

In a 50 mL flask are introduced 20 mL of acetone, then added NaH (2.8 mmol) and triethylamine (2.8 mmol) and the sulfonamide **7** (2 mmol). after stirring for 15 min at room temperature the sulfonyl chloride **2** (2 mmol) was

added. After stirring for 3 h at room temperature, the precipitate formed was filtered off and the filtrate was concentrated. The oil was triturated with 2×20 mL of Et₂O. After filtration, the solid was dissolved in 20 mL of CH₂Cl₂ and the solution was filtered. The solid obtained corresponds to the sodium salt, while the filtrate contained the ammonium salt of triethylamine **8**. The two solids were dried under vacuum.

The preparation of **9e-9f** and **10e-10f** was realized with 5.6 mmol of triethylamine without deprotonation with NaH. After 3 days stirring at room temperature and the same workup as previously the ammonium salt **8** was obtained.

Then in a 25 mL flask under nitrogen, the ammonium of bis(sulfonyl)imide **8** (1 mmol) were dissolved in 15 mL of THF. Sodium or lithium metal (1.1 mmol) was added to the solution and after 18 h at room temperature the mixture was filtered off. The solid phase was triturated with 2×10 mL of acetonitrile and then dried under vacuum.

9a: *N*-(*p*-tolylsulfonyl)-*p*-toluenesulfonamide lithium salt

¹H NMR (200 MHz, DMSO-D₆) δ 7.50 (d, *J* = 8.2 Hz, 4H), 7.13 (d, *J* = 7.9 Hz, 4H), 2.30 (s, 6H).

¹³C NMR (50 MHz, DMSO-D₆) δ 143.86 (s), 139.42 (s), 128.10 (s), 125.81 (s), 20.78 (s).

10a: *N*-(*p*-tolylsulfonyl)-*p*-toluenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 7.49 (d, *J* = 8.1 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 2.29 (s, 6H).

¹³C NMR (50 MHz, DMSO-D₆) δ 143.64 (s), 139.50 (s), 128.08 (s), 126.07 (s), 20.78 (s).

9b: *N*-(*p*-tolylsulfonyl)-*m*-nitrobenzenesulfonamide lithium salt

¹H NMR (200 MHz, DMSO-D₆) δ 8.28 – 8.15 (m, 2H), 8.02 (d, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.27 (s, 3H).

¹³C NMR (50 MHz, DMSO-D₆) δ 143.59 (s), 141.00 (s), 133.39 (s), 130.75 (s), 129.18 (s), 126.92 (s), 125.39 (s), 21.61 (s).

10b: *N*-(*p*-tolylsulfonyl)-*m*-nitrobenzenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 8.28 – 8.12 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 8.3 Hz, 2H), 2.24 (s, 3H).

¹³C NMR (50 MHz, DMSO-D₆) δ 143.45 (s), 140.90 (s), 133.42 (s), 130.79 (s), 129.16 (s), 127.02 (s), 125.51 (s), 21.62 (s).

10c: *N*-(*p*-tolylsulfonyl)-*p*-fluorobenzenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 7.69 – 7.44 (m, 4H), 7.26 – 7.02 (m, 4H), 2.29 (s, 3H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -107.93 – -110.73 (m).

¹³C NMR (50 MHz, DMSO-D₆) δ 160.83 (s), 143.87 (s), 141.43 (s), 139.41 (s), 129.13 (s), 128.88 (s), 128.03 (s), 125.72 (s), 115.38 (s), 115.02 (s), δ, 20.78 (s).

10d: *N*-(methylsulfonyl)-*p*-nitrobenzenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 8.44 (s, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 2.79 (s, 3H).

¹³C NMR (50 MHz, DMSO-D₆) δ 148.40 (s), 147.03 (s), 132.58 (s), 129.89 (s), 124.68 (s), 120.97 (s), 42.77 (s).

9e: *N*-(trifluoromethanesulfonyl)-*m*-nitrobenzenesulfonamide lithium salt

¹H NMR (200 MHz, DMSO-D₆) δ 8.49 – 8.43 (m, 1H), 8.43 – 8.32 (m, 1H), 8.22 – 8.13 (m, 1H), 7.87 – 7.74 (m, 1H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -77.97 (s).

¹³C NMR (50 MHz, DMSO-D₆) δ 147.24 (s), 146.42 (s), 132.41 (s), 130.58 (s), 125.92 (s), 120.83 (s).

10e: *N*-(trifluoromethanesulfonyl)-*m*-nitrobenzenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 8.48 – 8.44 (m, 1H), 8.42 – 8.33 (m, 1H), 8.23 – 8.12 (m, 1H), 7.88 – 7.75 (m, 1H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -77.97 (s).

¹³C NMR (50 MHz, DMSO-D₆) δ 147.28 (s), 146.38 (s), 132.41 (s), 130.58 (s), 125.92 (s), 120.83 (s).

9f: *N*-(trifluoromethanesulfonyl)-*p*-fluorobenzenesulfonamide lithium salt

¹H NMR (200 MHz, DMSO-D₆) δ 7.86 – 7.72 (m, 2H), 7.37 – 7.21 (m, 2H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -77.92 (s), -109.17 – -109.35 (m).

¹³C NMR (50 MHz, DMSO-D₆) δ 160.82 (s), 141.41 (s), 129.03 (s), 128.85 (s), 115.48 (s), 115.03 (s).

10f: *N*-(trifluoromethanesulfonyl)-*p*-fluorobenzenesulfonamide sodium salt

¹H NMR (200 MHz, DMSO-D₆) δ 7.87 – 7.72 (m, 1H), 7.39 – 7.21 (m, 1H).

¹⁹F NMR (188 MHz, DMSO-D₆) δ -77.93 (s), -108.03 – -110.60 (m).

¹³C NMR (50 MHz, DMSO-D₆) δ 160.82 (s), 141.43 (s), 129.03 (s), 128.85 (s), 115.48 (s), 115.03 (s).

- Conductivity measurements.

An impedance spectrometer EG&G model 6310 was used; the amplitude of the ac signal was typically 20 mV at frequencies between 100 kHz and 1 Hz.

Solutions (0.01 mol/L) of Li⁺ and Na⁺-salts **5**, **6**, **9** and **10** were prepared in a glove box using dimethylsulfoxide (DMSO) as the solvent. The solutions were analyzed using a closed 1 cm³ conductivity cell with 1 cm² platinum electrode area at 25 °C.