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

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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 3 h. 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 2 h 30. 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, CDC13) 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, CDC13) δ 148.33 (s), 145.50 (s), 132.28 (s), 131.34 (s), 129.54 (s), 122.42 (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 precipitation 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).
Preparation of Li⁺ and 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-D6) 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).
19F NMR (188 MHz, DMSO-D6) δ -104.91 – -105.20 (m, 1F), -108.09 – -108.46 (m, 2F).
13C NMR (50 MHz, DMSO-D6) 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⁺ 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. 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 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. The two solids were dried under vacuum.

9a: N-(p-tolylsulfonyl)-p-toluene sulfonamide lithium salt

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 7.50 (d, J = 8.2 \text{ Hz, 4H}), 7.13 (d, J = 7.9 \text{ Hz, 4H}), 2.30 (s, 6H). \]

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

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.28 – 8.15 (m, 2H), 8.02 (d, 1H), 7.66 (d, J = 7.9 \text{ Hz, 1H}), 7.31 (d, J = 8.2 \text{ Hz, 2H}), 7.11 (d, J = 8.3 \text{ Hz, 2H}), 2.27 (s, 3H). \]

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

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.28 – 8.12 (m, 2H), 7.99 (d, J = 7.8 \text{ Hz, 1H}), 7.65 (d, J = 7.9 \text{ Hz, 1H}), 7.41 (d, J = 8.2 \text{ Hz, 2H}), 7.10 (t, J = 8.3 \text{ Hz, 2H}), 2.24 (s, 3H). \]

9c: N-(p-tolylsulfonyl)-p-fluorobenzenesulfonamide sodium salt

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.43 (s, 1H), 8.28 (d, J = 8.2 \text{ Hz, 1H}), 8.12 (d, J = 8.0 \text{ Hz, 1H}), 7.72 (t, J = 8.0 \text{ Hz, 1H}), 7.29 (s, 3H). \]

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

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.43 (s, 1H), 8.28 (d, J = 8.2 \text{ Hz, 1H}), 8.12 (d, J = 8.0 \text{ Hz, 1H}), 7.72 (t, J = 8.0 \text{ Hz, 1H}), 7.29 (s, 3H). \]

9d: N-(trifluoromethanesulfonyl)-m-nitrobenzenesulfonamide lithium salt

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.43 (s, 1H), 8.28 (d, J = 8.2 \text{ Hz, 1H}), 8.12 (d, J = 8.0 \text{ Hz, 1H}), 7.72 (t, J = 8.0 \text{ Hz, 1H}), 7.29 (s, 3H). \]

10d: N-(trifluoromethanesulfonyl)-m-nitrobenzenesulfonamide sodium salt

\[ ^1\text{H NMR (200 MHz, DMSO-D}_6) \delta 8.43 (s, 1H), 8.28 (d, J = 8.2 \text{ Hz, 1H}), 8.12 (d, J = 8.0 \text{ Hz, 1H}), 7.72 (t, J = 8.0 \text{ Hz, 1H}), 7.29 (s, 3H). \]
- **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.