SUPPORTING INFORMATION

1-(Alkyl/Arylthiocarbamoyl)benzotriazoles as Stable Isothiocyanate Equivalents: Synthesis of Di- and Trisubstituted Thioureas

Alan R. Katritzky, Stephane Ledoux, Rachel M. Witek, and Satheesh K. Nair

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida,
Gainesville, FL 32611-7200

Table of Contents

1. Characterization Data for compounds 4b , 4f , and 4g	S2
2. Characterization Data for compounds 5c , 5i , 5k , 5m and 15	S3
3. Copies of NMR spectra for compounds 4b , 4f , and 4g	S5
4. Copies of NMR spectra for compounds 5c , 5i , 5k , 5m and 15	S9

Spectral Data of Thiocarbamoylbenzotriazoles 4b, 4f, and 4g

Benzotriazole-1-carbothioic acid (1,5-dimethylhexyl)amide (4b): Yellow oil, 99%. ^1H NMR (CDCl_3) δ 0.86 (d, 6H, J = 6.6 Hz), 1.20–1.28 (m, 2H), 1.39–1.81 (m, 8H), 4.66–4.71 (m, 1H), 7.45–7.50 (m, 1H), 7.62–7.67 (m, 1H), 8.09 (d, 1H, J = 8.2 Hz), 8.90–8.95 (m, 2H). ^{13}C NMR (CDCl_3) δ 19.5, 22.5, 23.7, 27.8, 36.2, 38.6, 51.0, 116.2, 120.2, 125.6, 130.2, 132.5, 147.1, 173.4. Anal. Calcd For $\text{C}_{15}\text{H}_{22}\text{N}_4\text{S}$: C, 62.03; H, 7.64; N, 19.29. Found: C, 62.48; H, 7.70; N, 19.52.

Benzotriazole-1-carbothioic acid [(*R*)-1-phenylethyl]amide (4f): Yellow oil, 99%. ^1H NMR (CDCl_3) δ 1.77 (d, 3H, J = 7.2 Hz), 5.74–5.84 (m, 1H), 7.30–7.50 (m, 6H), 7.61–7.66 (m, 1H), 8.09 (d, 1H, J = 8.2 Hz), 8.90 (d, 1H, J = 8.5 Hz), 9.32 (d, 1H, J = 6.3 Hz). ^{13}C NMR (CDCl_3) δ 21.0, 54.1, 116.1, 120.2, 125.7, 126.5, 128.0, 128.9, 130.3, 132.5, 141.1, 147.1, 173.4. Anal. Calcd For $\text{C}_{15}\text{H}_{14}\text{N}_4\text{S}$: C, 63.80; H, 5.00; N, 19.84. Found: C, 64.06; H, 4.93; N, 20.29.

Benzotriazole-1-carbothioic acid 4-methoxybenzylamide (4g): White needles, 97%, mp 82–83 °C. ^1H NMR (CDCl_3) δ 3.81 (s, 3H), 4.95 (d, 2H, J = 5.4 Hz), 6.91 (dd, 2H, J = 6.6, 2.1 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.44–7.50 (m, 1H), 7.62–7.69 (m, 1H), 8.07 (d, 1H, J = 8.1 Hz), 8.92 (d, 1H, J = 8.4 Hz), 9.25 (br s, 1H). ^{13}C NMR (CDCl_3) δ 48.6, 55.3, 114.3, 116.0, 120.2, 125.6, 127.5, 129.7, 130.3, 132.4, 147.0, 159.6, 174.1. Anal. Calcd For $\text{C}_{15}\text{H}_{14}\text{N}_4\text{OS}$: C, 60.38; H, 4.73; N, 18.78. Found: C, 60.48; H, 4.49; N, 19.56.

Spectral Data of Thioureas **5c**, **5i**, **5k**, **5m**, and **15**

1-(4-Methoxybenzyl)-3-(1-methylbutyl)thiourea (5c): Yellow oil, 93%. ^1H NMR (CDCl_3) δ 0.88 (t, 3H, $J = 7.2$ Hz), 1.15 (d, 3H, $J = 6.6$ Hz), 1.20–1.50 (m, 5H), 3.81 (s, 3H), 4.05 (br s, 1H), 4.55 (br s, 2H), 5.56 (s, 1H), 5.94 (s, 1H), 6.89 (d, 2H, $J = 8.7$ Hz), 7.25 (d, 2H, $J = 7.5$ Hz). ^{13}C NMR (CDCl_3) δ 13.9, 19.0, 20.6, 38.9, 47.9, 50.2, 55.3, 114.3, 125.9, 128.9, 159.3, 180.7. Anal. Calcd For $\text{C}_{14}\text{H}_{22}\text{N}_2\text{OS}$: C, 63.12; H, 8.32; N, 10.52. Found: C, 63.50; H, 8.70; N, 11.41.

3-Allyl-1-methyl-1-phenethylthiourea (5i): Yellow oil, 92%. ^1H NMR (CDCl_3) δ 2.98 (t, 2H, $J = 7.5$ Hz), 3.05 (s, 3H), 4.00 (t, 2H, $J = 7.2$ Hz), 4.27 (t, 2H, $J = 5.4$ Hz), 5.14–5.22 (m, 2H), 5.23 (br s, 1H), 5.83–5.94 (m, 1H), 7.21–7.38 (m, 5H). ^{13}C NMR (CDCl_3) δ 33.8, 38.0, 48.5, 55.8, 116.8, 126.5, 128.6, 128.8, 134.2, 138.7, 181.6. Anal. Calcd For $\text{C}_{13}\text{H}_{18}\text{N}_2\text{S}$: C, 66.62; H, 7.74; N, 11.95. Found: C, 66.31; H, 7.79; N, 12.37.

Piperidine-1-carbothioic acid 4-methoxybenzylamide (5k): Yellow oil, 95%. ^1H NMR (CDCl_3) δ 1.65–1.68 (m, 6H), 3.81–3.81 (m, 7H), 4.82 (d, 2H, $J = 4.5$ Hz), 5.64 (br s, 1H), 6.91 (d, 2H, $J = 8.4$ Hz), 7.31 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3) δ 24.1, 25.3, 48.8, 49.8, 55.2, 114.0, 129.4, 130.1, 159.0, 180.9. Anal. Calcd For $\text{C}_{14}\text{H}_{20}\text{N}_2\text{OS}$: C, 63.60; H, 7.62; N, 10.60. Found: C, 63.09; H, 7.50; N, 11.31.

Piperidine-1-carbothioic acid (furan-2-ylmethyl)amide (5m): White needles (from EtOAc/Hexanes), 94%, mp 104–107 °C. ^1H NMR (CDCl_3) δ 1.66 (br s, 6H), 3.78–3.80 (m, 4H), 4.87 (d, 2H, $J = 4.8$ Hz), 5.64 (br s, 1H), 6.30–6.34 (m, 2H) 7.38 (s, 1H). ^{13}C NMR (CDCl_3) δ 24.2, 25.4, 43.1, 48.8, 108.0, 110.5, 142.2, 151.1, 181.0. Anal. Calcd For $\text{C}_{11}\text{H}_{16}\text{N}_2\text{OS}$: C, 58.90; H, 7.19; N, 12.49. Found: C, 58.35; H, 7.31; N, 12.28.

1-Butyl-1-methyl-3-[2-(4-methylbenzoyl)phenyl] thiourea (15): Yellow oil, 76%. ^1H NMR (CDCl_3) δ 0.98 (t, 3H, $J = 7.2$ Hz), 1.38–1.46 (m, 2H), 1.67–1.77 (m, 2H), 2.44 (s, 3H), 3.38 (s, 3H), 3.87 (br s, 2H), 7.05–7.11 (m, 1H), 7.28 (d, 2H, $J = 8.1$ Hz), 7.49–7.56 (m, 2H), 7.67 (d, 2H, $J = 8.1$ Hz), 8.72 (d, 1H, $J = 8.4$ Hz), 10.69 (s, 1H). ^{13}C NMR (CDCl_3) δ 13.9, 20.1, 21.7, 29.2, 53.7, 122.1, 125.0, 125.9, 129.0, 130.5, 132.4, 132.6, 135.5, 142.2, 143.6, 179.6, 199.1. Anal. Calcd For $\text{C}_{20}\text{H}_{24}\text{N}_2\text{OS}$: C, 70.55; H, 7.10; N, 8.23. Found: C, 70.19; H, 7.18; N, 8.64.

Figure 1 ^1H NMR of **4b**

Figure 2 ¹H NMR of 4f

Figure 3 ¹H NMR of 4g

Figure 4 ^1H NMR of 5c

Figure 5 ^1H NMR of **5i**

Figure 6 ¹H NMR of 5k

Figure 7 ¹H NMR of 5m

Figure 8 ¹H NMR of 15

Figure 9 ¹³C NMR of **4b**

Figure 10 ¹³C NMR of 4f

Figure 11 ^{13}C NMR of **4g**

Figure 12 ^{13}C NMR of 5c

Figure 13 ¹³C NMR of 5i

Figure 14 ¹³C NMR of 5k

Figure 15 ¹³C NMR of 5m

Figure 16 ^{13}C NMR of **15**