SUPPORTING INFORMATION

Facile Synthesis of Bis(crown ether)benzils: Perspective Building Blocks for Metal Ion Sensors

Leonid S. Kikot',^a Alexander Yu. Lyapunov,^a Tatiana Yu. Bogaschenko,^a Sergey S. Smola,^b
Catherine Yu. Kulygina,^a Tatiana I. Kirichenko*^a

^a *Department of Fine Organic Synthesis, A.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, 65080 Odessa, Ukraine*

^b *Department of Chemistry of Lanthanides, A.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorfskaya doroga 86, 65080 Odessa, Ukraine*

Fax: +38 0487659602

E-mail: kirichenko@physchem.od.ua

General Procedure for the Synthesis of Bis(crown ether)benzils 3a–c.

The corresponding stilbene **2a–c** (20 mmol) was dissolved in DMSO (100 mL) at 100–120 °C. The resulting solution was cooled to 80 °C and aqueous 48% HBr (20 mL) was added in one portion. The reaction mixture was stirred at 115 °C for 1.5 h. Water (120 mL) was added to the warm reaction mixture and the resulting slurry was cooled to r.t. The precipitate was filtered off, washed with water and air-dried. The crude product was purified by recrystallization from the appropriate solvent.

Bis(12-crown-4)benzil (3a). Thin colorless needles: 6.53 g, 65% yield; mp 179.5–180.5 °C (from BuOH). ¹H NMR (300 MHz, CDCl₃) δ 3.72–3.95 (m, 16 H), 4.19–4.30 (m, 8 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 7.57 (dd, *J* = 8.4, 1.9 Hz, 2 H), 7.68 (d, *J* = 1.9 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 69.4, 69.6, 70.4, 70.7, 71.3, 73.0, 115.4, 119.4, 127.0, 127.1, 150.2, 156.7, 192.8. MS (EI, 70 eV) *m/z* (%) 502 [*M*⁺] (3), 251 (100), 163 (40). Anal. Calcd for C₂₆H₃₀O₁₀ (502.51): C, 62.14; H, 6.02. Found: C, 62.31; H, 6.09.

Bis(15-crown-5)benzil (3b). Light-yellow needles: 7.20 g, 61% yield; mp 180.5–181.5 °C (from PhMe; lit.^{7b} 180–181 °C). MS (EI, 70 eV) *m/z* (%) 590 [*M*⁺] (8), 295 (100), 163 (38).

Bis(18-crown-6)benzil (3c). Light-yellow solid: 6.91 g, 51% yield; mp 146.5–147.5 °C (from MeOH). ¹H NMR (300 MHz, CDCl₃) δ 3.63–3.83 (m, 24 H), 3.88–4.01 (m, 8 H), 4.16–4.28 (m, 8 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 7.45 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.55 (d, *J* = 1.6 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 68.9, 68.9, 69.1, 69.2, 70.5, 70.5, 70.6, 70.7, 70.9, 70.9, 111.6, 112.2, 126.1, 148.8, 154.4, 193.3. MS (EI, 70 eV) *m/z* (%) 678 [*M*⁺] (11), 339 (100), 163 (37). Anal. Calcd for C₃₄H₄₆O₁₄ (678.72): C, 60.17; H, 6.83. Found: C, 59.94; H, 6.96.

2,3-Bis((benzo-15-crown-5)-3'-yl)quinoxaline (4)

Bis(15-crown-5)benzil **3b** (1.0 g, 1.7 mmol) and *o*-phenylenediamine (0.202 g, 1.87 mmol) were dissolved in ethanol (25 mL). Catalytic amount of PTSA was added and the mixture was refluxed for

12 h under Ar. Benzene (100 mL) was added to the cooled mixture and the solution was successively washed with water (2×40 mL), aqueous 1% HCl (2×20 mL), water (5×40 mL) and subjected to azeotropic drying. The solvent was removed at reduced pressure and the residue was subjected to column chromatography (SiO₂, eluent: CHCl₃–MeOH, 10:1). The crude product was purified by recrystallization from benzene/hexane mixture to give **4** as light-yellow crystals: 0.99 g, 89% yield; mp 146–147.5 °C. ¹H NMR (300 MHz, CDCl₃) δ 3.65–3.98 (m, 24 H), 3.99–4.24 (m, 8 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 7.02 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.18 (d, *J* = 1.6 Hz, 2 H), 7.73 (dd, *J* = 6.2, 3.4 Hz, 2 H), 8.14 (dd, *J* = 6.2, 3.4 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 68.8, 68.9, 69.4, 69.4, 70.3, 70.4, 71.0, 71.0, 113.1, 115.4, 123.4, 128.8, 129.5, 131.9, 140.8, 148.7, 149.8, 152.8. MS (FAB, Ar, 8 kV) *m/z* 663 [M+H⁺]. Calcd for C₃₆H₄₂N₂O₁₀ (662.73): C, 65.24; H, 6.39; N, 4.23. Found: C, 65.01; H, 6.46; N, 4.33.

¹H and ¹³C NMR spectra for Bis(12-crown-4)benzil **3a**

¹H and ¹³C NMR spectra for Bis(18-crown-6)benzil **3c**

¹H and ¹³C NMR spectra for Bis(crown ether) **4**