Supporting Information

Title: Competing hydrogen-bond and halogen-bond donors in crystal engineering

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1. General Experimental Details

^{1}H NMR spectra were recorded on a Varian Unity plus 400 MHz spectrometer spectrometer in $CDCl_3$. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or residual protiosolvent as internal reference and are reported as position (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons). Melting points were recorded on Fisher-Johns melting point apparatus and are uncorrected. Infrared spectroscopy (IR) was done on a Nicolet 380 FT-IR. Precursors 2,3,5,6-tetrafluoro-4-iodobenzaldehyde and 2,3,5,6-tetrafluoro-4-bromobenzaldehyde were synthesized following previously published methods.[1] 1,4-dibromo-2,3,5,6-tetrafluorobenzene was purchased from Matrix Scientific respectively. All the other chemicals were purchased from Sigma Aldrich and used without further purification, unless otherwise noted. Solvents and reagents were purified according to the procedures outlined by Perrin and Armarego. [Purification of Laboratory Chemicals; D. D. Perrin, W.L.F. Armarego; 3rd Ed., Pergamon Press, 1988].

2. Experimental Procedures and Product Characterization Data

2.1. Synthesis of COOH-I

To oven dried one-necked round-bottomed flask with stir bar added 1,4-diiodo-2,3,5,6-tetrafluorobenzene (1 g, 2.5 mmol) under stream of Argon and sealed the flask with rubber septum. To this flask was added dry, freshly distilled THF (70 ml) via canula. The solution was cooled down to -78 °C by immersing into dry ice-acetone bath for 15 mins. To this solution was then slowly added *n*-butyllithium (1.6 M solutions in hexanes, 1.65 ml, 2.6 mmol). After 20 minutes, carbon dioxide gas was purged into reaction mixture for 15 mins followed by addition of excess solid dry ice to reaction mixture. The reaction mixture was slowly warmed to 0 °C and quenched with 2M HCl carefully. Solvent was removed on rotary evaporator and the product was extracted in methylene chloride. The organic phase was washed with saturated sodium thiosulfate solution, brine solution and dried using anhydrous magnesium sulfate. The solvent was removed on rotary evaporator to yield crude product which was triturated with cold hexane and filtered off to yield pure **COOH-I** (0.414g, 52% yield). Dec. 140 ºC and all other characterization data matches with previously reported data.[2]

2.2. Synthesis of COOH-Br

Prepared according to procedure used to synthesize **COOH-I** starting with 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1 g, 3.2 mmol), after aqueous work up, pure **COOH-Br** was obtained (0.764g, 86% yield). M.p. 128-130 ºC and all other characterization data matches with previously reported data.2

2.3. Synthesis of Ox-I

1-Iodo-2,3,5,6-tetrafluoro benzaldehyde (600 mg, 1.97 mmol), Hydroxylamine hydrochloride (274 mg, 3.98 mmol) and sodium hydroxide (159 mg, 3.98 mmol) were added in ceramic mortar and pestle, to this mixture 4-5 drops of ethanol were added and grinded at room temperature for 5 minutes. The solid was filtered, washed with water and air-dried, yielding a pure compound **Ox-I**, (674 mg, 90 %). Dec. ~240 ºC; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 9.00 (br s, 1H), 8.26 (s, 1H). All other characterization data matches with previously reported data.[3]

2.4. Synthesis of Ox-Br

1-Bromo-2,3,5,6-tetrafluoro benzaldehyde (1 g, 3.89 mmol), Hydroxylamine hydrochloride (537 mg, 7.78 mmol) and sodium hydroxide (311 mg, 7.78 mmol) were added in ceramic mortar and pestle, to this mixture 4-5 drops of ethanol were added and grinded at room temperature for 5 minutes. The solid was filtered, washed with water and air-dried, yielding a pure compound **Ox-Br**, (935 mg, 88 %). Dec. ~138 ºC; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.35 (br s, 1H), 8.26 (s, 1H). All other characterization data matches with previously reported data.3

2.5. Synthesis of OH-I

Iodopentafluorobenzene (1.47 g, 4.95 mmol) was added in lots over 30 minutes to the mixture of potassium hydroxide (0.7 g, 12.5 mmol) in *t*-butanol (10 mL) at 65 °C under constant stirring. After the addition, the temperature of the reaction was raised to reflux and maintained for 6 hours. After the completion of reaction, reaction was quenched by water and *t*-butanol was removed under vacuum. The aqueous layer was extracted with methylene chloride (3x25 mL) to remove any unreacted Iodopentafluorobenzene. The aqueous layer was then acidified with conc. hydrochloric acid (5 mL) and extracted with methylene chloride (3x25 mL). The organic phase was dried over magnesium sulfate and solvent removed under vacuum to yield crystalline solid **I-OH** (1.16 g, 80%). M.p. 42-44 ºC and all other characterization data matches with previously reported data.[4]

3. References:

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