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Supporting information for article:

C—I···N and C—I···π halogen bonding in the structures of 1-benzyl-iodoimidazole derivatives

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S1.

S2. Experimental

S2.1. 1-Benzyl-4-iodo-1H-imidazole, 2. A suspension of NaH (60% in mineral oil, 0.401 g, 10.0 mmol) in 8 mL hexane was stirred under argon for 5 mins. After removal of the supernatant solution, anhydrous THF (10 mL) was then added. The mixture was cooled to 0 ºC and a solution of 4(5)-iodo-1H-imidazole (1.48 g, 7.64 mmol) in THF (7 mL) was added to the resulting NaH suspension. The entire mixture was allowed to stir for 40 mins at room temperature. The mixture was again cooled to 0 ºC, followed by addition of benzyl bromide (0.95 mL, 1.37 g, 7.99 mmol). The mixture was stirred at 0 ºC for 20 mins and for further 20 mins at room temperature. The reaction was quenched with saturated NH_4Cl (30 mL) and the solution was concentrated. The residue was extracted with CH_2Cl_2 (2 x 50 mL), and the solution was subsequently washed with H_2O (60 mL), brine (100 mL), dried over Na_2SO_4 and concentrated to give yellow oil (2.54 g). The crude product was isomerized by reaction with a slight excess of benzyl bromide. Thus 2.54 g of the product was dissolved in DMF (20 mL) and benzylbromide (0.1 mL, 10 mmol %) added. The mixture was stirred at 75 ºC for 24 hrs. The reaction was quenched with 2 mL of H_2O, and dissolved with CH_2Cl_2 (200 ml). The DMF was removed by washing the organic layer with H_2O (7 x 200 mL). The organic was dried over Na_2SO_4 and the solvent removed *in vacuo*. The product was recrystallized from (CH_3CN/EtOH: 1/2). Mp 97-102 ℃, Lit. (Lovely, 2007), 99-100 ℃. ^{1}H NMR ($CDCl_3$) δ 5.08 (s, 2H), 6.97 (s, 1H), 7.17 (dd, *J* = 2.0 Hz, 7.8 Hz, 2H), 7.34-7.38 (m, 3H) 7.44 (s, 1H).

S2.2. 1-Benzyl-1H-benzoimidazole. A suspension of NaH (60% in mineral oil, 1.53 g, 37.71 mmol) in 20 mL hexane was stirred under argon for 5 mins. After removal of the supernatant solution, anhydrous THF (20 mL) was then added. The mixture was cooled to 0 ºC and a solution of 1-benzy-1H-benzoimidazole (3.6 g, 30.47 mmol) in THF (24 mL) was added to the resulting NaH suspension. The entire mixture was allowed to stir for 40 mins at room temperature. The mixture was again cooled to 0 ºC, followed by addition of benzyl bromide (3.8 mL, 5.47 g, 31.99 mmol). The entire mixture was stirred at 0 ºC for 20 mins and then at room temperature for 15 mins. The reaction was quenched with saturated NH_4Cl (40 mL) and the THF was concentrated. The residue was extracted with CH_2Cl_2 (2 x 40 mL), and the solution was subsequently washed with H_2O (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography with a mixture of 1:10 EtOAc and Hexane as the eluent. The product was isolated as an off-white solid (4.64 g, 72%) which was recrystallized from 3:2 Hexane/EtOAc. Rf = 0.45 (Hexane/EtOAc: 1/1); mp = 116.5-117.8 ºC. ^{1}H NMR consistent with that reported by Lygin and de Meijere (2009).

S2.3. **1-Benzyl-2-iodo-1H-benzoimidazole, 3**. 1-Benzyl benzoimidazole (4 g, 19.21 mmol) and anhydrous THF (60 mL) were combined in a flask under argon. The mixture was cooled to -78 ºC and stirred at this temperature for 10 mins. 1.6 M n-BuLi (12 mL, 19.21 mmol, 1 equiv.) was added slowly over 2 minutes. It was left to stir at -78 ºC for 45 mins. I_2 (7.31 g, 28.81 mmol, 1.5 equiv.) was crushed and added into the mixture, and the entire mixture was allowed to stir at room temperature for 3 hrs under argon. The mixture was extracted with CH_2Cl_2 (300 mL) and the excess I_2 was quenched with 10% Na_2SO_3 (200 mL). The organic layer was separated, washed with H_2O (200 mL) and brine (100ml x 2), and dried over Na_2SO_4. The solvent was removed in vacuo and the crude product purified by flash column chromatography (Hexane/EtOAc: 10/1), Rf = 0.8 (Hexane/EtOAC: 1/1) to afford a white solid (3.51 g, 54% yield). The solid was then recrystallized from (Hexane/EtOAc: 3/2); m p = 121-122 ºC, lit. 112-113 ºC (O'Connell *et al.* 2012). ^{1}H NMR consistent with that reported by O'Connell et al. (2012).

Table S1 Comparison of the observed torsional angles in structures **1, 2** and **3** and torsional angles in the optimized gas phase structure calculated using Spartan '10.

Compound	**Torsional angle[a]**	**Crystal data (º)**	**Optimized Structure (º)**
1	C1-N1-C4-C5	-89.3(3)	-106.30
	C3-N1-C4-C5	90.2(3)	72.29
	N1-C4-C5-C6	13.0(4)	27.76
	N1-C4-C5-C10	-167.7(2)	-154.71
2	C1 N1 C4 C5	123.20(19)	119.79
	C3 N1 C4 C5	-56.5(3)	-62.47
	N1 C4 C5 C10	129.69(19)	118.79
	N1 C4 C5 C6	-52.0(2)	-62.09
3	C1 N1 C8 C9	93.38(19)	110.58
	C7 N1 C8 C9	-77.17(19)	-72.00
	N1 C8 C9 C14	-13.4(2)	-40.68
	N1 C8 C9 C10	167.25(14)	141.89

[a] Numbering scheme as shown in Figures 2, 3 and 4.

References

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