Supporting Information File 1

Experimental Section

Inversion symmetry and local vs. dispersive interactions in the nucleation of hydrogen bonded cyclic n-mer and tape of imidazolecarboxamidines

Sihui Long, Venkatraj Muthusamy, Peter G. Willis, Sean Parkin and Arthur Cammers*

Address: University of Kentucky, Department of Chemistry, Lexington, KY. 40506-0055
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Experimental Section

General. Melting points are uncorrected. IR spectra were recorded using FT-IR Nicolet 560 spectrometer. NMR spectra were obtained on a Varian Gemini and Varian INOVA spectrometers at $^1$H observation frequencies 200 and 400 MHz. NMR spectra for characterization purposes taken in CDCl$_3$ were complicated due to broadening by aggregation and slow exchange of amidine rotamers; DMSO-d$_6$ clarified some of these. Solvent-dependent kinetics were previously investigated [1].

$N,N'$-Ditolyl-4,5-dimethylimidazole-1-carboxamidine 5b. A mixture of 4,5-dimethylimidazole (85 mg, 0.88 mmol) and $N,N'$-di-tolylcarbodiimide (210 mg, 0.94 mmol) was refluxed in 10 mL of THF for 12 h. THF was evaporated and the residues were fractionated by flash chromatography: EtOAc ($R_f = 0.42$), to afford a white solid. Suitable crystals were obtained from EtOAc via slow evaporation. 200 mg (71%); mp 150–153 °C; IR (cm$^{-1}$) 1662, 1607, 1553, 1505; $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 9.62 (bs, 1H), 7.64 (bd, $J = 8.0$ Hz, 2H), 7.52 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.0$ Hz, 2H), 6.50 (d, $J = 8.0$ Hz, 2H), 6.26 (s, 3H), 2.18 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz): $\delta$ 145.1, 139.0, 137.6, 135.1, 132.7, 132.0, 131.0, 129.8 (br. exchange), 124.3, 122.4, 122.0, 119.9, 20.9 (br. exchange), 12.6, 9.1; MS (EI) $m/z$ 317([M-H]$^+$); C$_{20}$H$_{22}$N$_4$ (318)

Analogous methods afforded the compounds below.
**N,N′-Dicyclohexyl-4,5-dimethylimidazole-1-carboxamidine 5c.** Flash chromatography: EtOAc ($R_f = 0.35$). 200 mg (53%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 122–125 °C; IR (cm⁻¹) 3254.0, 2925.7, 2851.5, 1666.7, 1580.6, 1524.3; ¹H NMR (CDCl₃, 400 MHz) δ 7.306 (s, 1H), 2.169 (s, 3H), 2.081 (s, 3H), 2.0–1.5 (m, 10H), 1.5-1.0 (m, 10H); ¹³C NMR (CDCl₃, 100 MHz) δ 133.577, 133.372, 121.394, 34.971, 33.931, 25.855, 25.088, 24.974, 24.777, 12.737, 8.502; MS (EI) m/z 302 (M⁺); C₁₈H₃₀N₄ (302).

**N,N′-Ditolyl-2-methylimidazole-1-carboxamidine 6b.** Flash chromatography: EtOAc ($R_f = 0.38$), to afford 150 mg (81%) of a white solid. Crystals were obtained by slow evaporation of EtOAc. mp 138–141 °C; IR (cm⁻¹) 1655, 1625, 1556, 1532; ¹H NMR (400 MHz, CDCl₃) δ 7.1–6.8 (m, 10H), 6.5 (bs, 1H) 2.28 (s, 3H), 2.20 (bs, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 130.3, 130.0 128.1, 124.1, 120.8, 119.0, 21.2, 14.3; MS (EI) m/z 304 (M⁺); C₁₉H₂₀N₄ (304).

**N,N′-Dicyclohexyl-2-methylimidazole-1-carboxamidine 6c.** Flash chromatography: EtOAc, to afford 300 mg (50%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 140–142 °C; IR (cm⁻¹) 1672, 1531; ¹H NMR (400 MHz, CDCl₃) δ 6.90 (bs, 1H), 6.79 (bs, 1H), 4.1–3.0 (bm, 3H), 2.30 (s, 3H), 1.8–1.0 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 140.0 br, 128.0, 118.3, 58-50 br, 25.8, 24.8, 13.1; MS (EI) m/z 288 (M⁺); C₁₇H₂₈N₄ (288).

**N,N′-Diisopropyl-2,4,5-trimethylimidazole-1-carboxamidine 7a.** Flash chromatography EtOAc ($R_f = 0.1$), to afford 100 mg (52%) of a white solid. Crystals were obtained by slow evaporation in hexane. mp 120–123 °C; IR (cm⁻¹) 1659, 1533; ¹H NMR (CDCl₃,
400 MHz) δ 3.8 (bs, 1H), 2.9 (s, 1H), 2.28 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.11 (br, 10H); 13C NMR (CDCl3, 100 MHz) δ 141.3, 132.4, 121.1, 13.3, 12.5, 8.8; MS (EI) m/z 236 (M+); C13H24N4 (236).

N,N’-Ditolyl-2,4,5-trimethylimidazole-1-carboxamidine 7b. Flash chromatography EtOAc (Rf = 0.28), to afford 87 mg (72%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 176–178 °C; IR (cm⁻¹) 1659, 1606, 1553; 1H NMR (CDCl3, 400 MHz) δ 8.6–6.2 (br, 8H), 2.28 (br, 6H), 2.13 (br, 3H), 2.07 (br, 3H), 2.00 (br, 3H); 13C NMR (CDCl3, 100 MHz) δ 141.3, 132.4, 121.1, 13.3, 12.5, 8.9; MS (EI) m/z 332 (M+); C21H24N4 (332).

N,N’-Dicyclohexyl-2,4,5-trimethylimidazole-1-carboxamidine 7c. Flash chromatography, eluting with EtOAc (Rf = 0.15), to afford 380 mg (88%) of a white solid. Crystals were obtained by slow evaporation of EtOAc/Hexane. mp 132–134 °C; IR (cm⁻¹) 1664.08, 1525.84; 1H NMR (CDCl3, 400 MHz) δ 3.85 (s, 1H), 2.95 (bs, 2H), 2.25 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.8–1.4 (m, 10H), 1.4–1.0 (br, 10H); 13C NMR (CDCl3, 100 MHz) δ 141.3, 139.5, 132.2, 121.1, 56.9 br, 50.0 br, 35.1 br, 34.9 br, 25.8, 25.5 br, 24.8, 13.3, 12.6, 8.9 MS (EI) m/z 316 (M+); C19H32N4 (316).

N,N’-Diisopropyl-4,5-diphenylimidazole-1-carboxamidine 8a. Upon cooling much 4,5-diphenylimidazole precipitated from solution. Flash chromatography: EtOAc (Rf = 0.49), 80 mg (29%) as a white solid. Crystals were grown in EtOAc. mp 169–171 °C; IR (cm⁻¹) 1673, 1618, 1577, 1526; (NMR DMSO-d6: multiple species present) 1H NMR (CDCl3, 400 MHz) δ 7.56 (s, 1H), 7.51–7.16 (m, 10H), 3.8–3.0 (bm 2H), 1.24–0.90 (bm, 10H);
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.1, 135.9, 134.1, 129.9, 128.8, 128.7, 128.4, 127.5, 127.1, 29.9, 22.8 br; MS (EI) m/z 346 (M$^+$); C$_{22}$H$_{28}$N$_4$ (346).

_N,N'-Ditolyl-4,5-diphenylimidazole-1-carboxamidine 8b._ Flash chromatography: CH$_2$Cl$_2$ forerun followed by 10:1 CH$_2$Cl$_2$: EtOAc, to afford 120 mg (36%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 142–145 °C; IR (cm$^{-1}$) 1658.82, 1604.23, 1504.90; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.1–6.7 (br, m, 19H), 6.05 (br, 1H), 2.23 (br, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.8, 130.3, 130.2, 129.6, 129.2, 129.0, 128.6, 128.4, 128.3, 127.7, 127.5, 127.2, 120.9, 21.0; MS (EI) m/z 442(M$^+$); C$_{30}$H$_{26}$N$_4$ (442).

_N,N'-Diisopropylimidazole-1-carboxamidine 9a._ Imidazole (0.07 g, 1 mmol) and _N,N'-diisopropylcarbodiimide_ (0.18 g, 1.2 mmol) were refluxed in THF (4 mL) for 12 h. Upon cooling, crystals of 9a formed and were collected by filtration. Recrystallization from hexane afforded colorless crystals (0.14 g, 72 %); mp 75–77 °C; IR (cm$^{-1}$) 1672, 1559; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (br s, 1H), 7.58 (br s, 2H), 7.22 (br s, 1H), 7.11 (br s, 2H), 7.06 (br s, 1H), 7.00 (br s, 2H), 3.2–3.8 (m, 9H), 1.2–1.1 (br s, 36 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ; 144.2, 139.0, 136.5, 129.5, 118.3, 48.9 (b), 43.7 (b), 24.0 (b); MS (EI) m/z 194(M$^+$); C$_{10}$H$_{18}$N$_4$ (194.28).

Analogous methods afforded the compounds below.

_N,N'-Ditolylimidazole-1-carboxamidine 9b._ Diffraction-quality crystals were obtained upon cooling in EtOAc, toluene, ether, CH$_3$CN, iso-propyl ether, or cholorbenzene. (0.22 g, 76 %); mp 122–124 °C; IR (cm$^{-1}$) 1664, 1555; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (br s, 1H), 7.03 (m, 8H), 6.66 (br s, 2H), 6.22 (br s, 1H), 2.28 (br s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.2, 139.0, 136.5, 129.5, 118.3, 48.9 (b), 43.7 (b), 24.0 (b); MS (EI) m/z 194(M$^+$); C$_{10}$H$_{18}$N$_4$ (194.28).
MHz, CDCl$_3$) δ; 137.0, 130.2, 129.8, 129.6, 124.1, 121.4, 118.3, 21.2; MS (EI) m/z 290(M$^+$); C$_{18}$H$_{18}$N$_4$ (290.37).

**N,N$'$-Dicyclohexylimidazole-1-carboxamidine** 9c. Diffraction-quality crystals were obtained upon cooling in EtOAc. (0.19 g, 70 %); mp 130–132 °C; IR (cm$^{-1}$) 3275, 1675, 1530, 1487; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (br s, 2H), 7.00 (br s, 1H), 3.10 (br s, 2H), 1.9–1.0 (m, 21H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ; 136, 129, 118, 34.6, 33.8, 25.8, 25.6, 24.9, 24.6; MS (EI) m/z 274(M$^+$); C$_{16}$H$_{26}$N$_4$ (274.41).

**N,N$'$-Ditolylbenzimidazole-1-carboxamidine** 10b. Flash chromatography: 6:1 CH$_2$Cl$_2$/EtOAc, to afford 270 mg (78%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 159–160 °C; IR (cm$^{-1}$) 1665.88, 1606.21, 1549.98; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.2–6.4 (m, 13H), 2.27 (br, 6H); $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 9.87 (s, 1H), 8.29 (s, 1H), 7.62–7.67 (m, 2H), 7.40 (d, $J = 7.1$, 1H), 7.19–7.26 (m, 3H), 7.16 (d, $J = 7.4$, 2H), 6.82 (d, $J = 7.1$, 2H), 6.52 (d, $J = 7.4$, 2H), 2.28 (3H), 2.09 (3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 142.1, 130.4, 124.8, 123.9, 121.1, 120.6, 21.0; $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ 144.8, 142.8, 142.1, 137.9, 137.3, 132.4, 131.8, 131.1, 130.3, 129.1, 123.8, 123.6, 122.6, 121.0, 119.6, 119.3, 111.6, 20.5, 20.3 (methyl signals exchange at 25°C); MS (EI) m/z 340 (M$^+$); C$_{22}$H$_{20}$N$_4$ (340).

**N,N$'$-Dicyclohexylbenzimidazole-1-carboxamidine** 10c. Flash chromatography: EtOAc ($R_f = 0.5$), 285 mg (86%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 114–117 °C; IR (cm$^{-1}$) 1665.33, 1613.42, 1529.56; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.2–7.3 (m, br, 5H), 4.09 (br, 1H), 3.22 (br, 1H), 2.90 (br, 1H), 1.90–1.00 (m, 20H); The chemical shifts and coupling in the ABMX portion of the following spectrum
were extracted via simulation, gNMR v. 4.1.0, 1999. $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 8.26 (s, 1H), 7.72 (d, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.31 (dd, $J = 7.7$, 7.3 Hz, 1H), 7.26 (dd, $J = 7.7$, 7.4 Hz, 1H), 6.68 (d, $J = 7.1$ Hz, 1H, NH), 2.07–1.95 (m, 2H), 1.79–1.66 (m, 4H), 1.62–1.52 (m, 4H), 1.49–1.35 (m, 4H), 1.32–1.14 (m, 8H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ 156.6, 142.2, 138.5, 133.1, 123.4, 122.2, 119.6, 110.7, 56.1, 49.8, 35.1, 31.7, 25.6, 25.2, 24.5, 24.1; MS (EI) $m/z$ 324 (M$^+$); C$_{20}$H$_{28}$N$_4$ (324).

$N,N'$-Diisopropyl-2-methylbenzimidazole-1-carboxamidine, 11a. Crystals were obtained by slow evaporation in EtOAc. (0.96 g, 74%); mp 124–126 °C; IR (cm$^{-1}$) 1657, 1537; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, $J = 2.8$ Hz, 1H), 7.26 (br s, 3H), 3.99 (br s, 1H), 2.87 (br s, 1H), 2.57 (s, 3H), 1.3-1.1 (br s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ; 149.8, 142.1, 138.5, 134.2, 122.9, 122.5, 119.0, 109.7, 48.7(b), 43.5(b), 24.5(b), 13.5; MS (EI) $m/z$ 258(M$^+$); C$_{15}$H$_{22}$N$_4$ (258.37).

$N,N'$-Ditolyl-2-methylbenzimidazole-1-carboxamidine 11b. Flash chromatography: EtOAc, 250 mg (70%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 199–200 °C; IR (cm$^{-1}$) 1651, 1604, 1546; The chemical shifts and coupling in the ABMX portion of the following spectrum were extracted via simulation. $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 9.83 (s, 1H), 7.73–7.67 (m, 2H), 7.51 (dd, $J = 8.0$, 1.9 Hz, 1H), 7.38 (dd, $J = 8.0$, 1.9 Hz, 1H), 7.18 (dd, $J = 8.1$, 7.4 Hz, 1H), 7.16 (dd, $J = 8.0$, 7.4 Hz, 1H), 7.19–7.14 (m, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.49 (d, $J = 8.0$ Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 149.9, 144.4, 141.8, 137.9, 137.3, 134.5, 131.9, 131.4, 129.2, 129.1, 122.8, 122.2, 121.0, 119.2, 118.5, 110.6, 20.5, 20.2, 14.2; MS (EI) $m/z$ 354(M$^+$); C$_{23}$H$_{23}$N$_4$ (354).
N,N'-Dicyclohexyl-2-methylbenzimidazole-1-carboxamidine 11c. Flash chromatography: EtOAc ($R_f$ = 0.5), 235 mg (77%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 152–155 °C; IR (cm$^{-1}$) 1663.02, 1529.85; $^1$H NMR (DMSO-$d_6$, 400 MHz) δ 7.57 (dm, $J = 6.2$ Hz, 1H), 7.23-7.16 (m, 2H), 7.21 (s, 1H), 6.65 (d, $J = 7.51$ Hz, 1H), 3.64 (s, 1H), 2.42 (s, 3H), 2.40–2.33 (m, 1H), 2.07–1.94 (m, 2H), 1.78–1.64 (m, 2H), 1.64–1.48 (m, 2H), 1.47–0.72 (m, 14H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.2, 142.5, 134.5, 123.2, 122.8, 119.3, 110.8, 110.0, 97.2 (br), 52.8, 50.5, 35.1 (br), 34.2, 33.9, 33.0 (br), 25.9, 25.7, 25.3, 25.2, 24.8, 13.9; $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 149.8, 141.9, 138.6, 134.5, 122.4, 121.8, 118.4, 109.7, 56.1, 49.6, 35.0, 34.8, 31.7, 31.5, 25.6, 25.2, 24.5, 24.1, 13.4; MS (EI) m/z 338(M$^+$); C$_{21}$H$_{30}$N$_4$(338).

The following compounds were not included in the argument due to the involvement of the amino group at the 2-position of the imidazole moiety in hydrodorgen bonding. The focus of this work was a solid state involving imidazole as a hydrogen bond acceptor and amidine as a hydrogen bond donor. In one case, the 2-amino group participated in the chemistry of the addition, giving rise to an unexpected product.

2-Amino-N,N'-Diisopropylbenzimidazole-1-carboxamidine 12a. A mixture of 2-amino-benzimidazole (1.11 g, 8.31 mmol) and the N,N'-diisopropylcarbodiimide (3.7 g, 16.6 mmol) was dissolved in THF (20 mL) and the solution was refluxed for 12 h. Crude product was extracted from water into CHCl$_3$. Recrystallization of the residue from ethyl acetate afforded colorless crystals (1.82 g, 85 %); IR (cm$^{-1}$) 1770, 1554; $^1$H NMR (300 MHz, CDCl$_3$) δ; 7.40 (d, 1H), 7.27 (br d, 1H), 7.14 (t, 1H), 7.05 (t, 1H), 5.2–6.0 (br s, 2H), 3.2–4.2 (br m, 4H), 1.0–1.4 (br s, 12H); $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ; 160.6, 153,
141.9, 133.1, 122.6, 116.7, 109.7 (b), 47.0 (b), 24.1 (b); Analysis calculated for C\(_{14}H_{21}N_5\) (259.35): C 64.83; H 8.16; N 27.01; found: C 64.51; H 8.31; N 26.55.

2-Amino-N,N'-diisopropyl-5,6-dimethylbenzimidazole-1-carboxamidine **13a.** mp 195–197 °C; IR (cm\(^{-1}\)) 1651, 1552; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.17 (s, 1H), 7.03 (s, 1H), 5.36 (br s, 2H), 3.8–3.4 (m, 2H), 2.31 (s, 6H), 1.25–1.13 (br s, 12H); \(^1^3\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\); 163.7, 152.5, 140.0, 131.0, 129.0, 117.3, 110.5 (vb), 47.2 (vb), 24.2 (b), 20.5; MS (EI) m/z 287(M\(^+\)); C\(_{16}H_{23}N_5\) (287.4).

7,8-Dimethyl-2-tolylamino-4-(tolylimino)-3-tolyl-[1,3,5]triazino[1,2-a]benzimidazole **14b.** (Figure 12) Flash chromatography: EtOAc 350 mg (87%) of a white solid. Crystals were obtained by slow evaporation in EtOAc. mp 163–165 °C; IR (cm\(^{-1}\)) 3398, 1686, 1632, 1598(s), 1561, 1528, 1509; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (s, 1H), 7.50 (s, 1H), (Tol. o-cplg. analyzed as doublets) 7.36 (d, 2H, \(J = 9.0\) Hz), 7.06 (d, 2H, \(J = 9.0\) Hz), 7.05 (d, 2H, \(J = 8.4\) Hz), 7.00 (d, 2H, \(J = 8.4\) Hz), 6.72 (d, 2H, \(J = 8.0\) Hz), 6.31 (d, 2H, \(J = 8.0\) Hz), 6.13 (br, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.1, 149.6, 143.3, 141.0, 141.7 (br), 134.7, 134.4, 133.4, 132.0, 131.7, 131.1, 131.0, 130.6, 130.5, 129.6, 128.8, 128.4, 121.4, 120.8, 118.6, 115.9, 21.3, 21.0, 20.8, 20.6, 20.5; MS (EI) m/z 499(M+); C\(_{32}H_{30}N_6\)(calc. 499.2); 500(M+1, rel. int. 37.4%, calc. 37.2%); 501(M+2, rel. int. 7.1%, calc. 6.8%).

![Figure 12. Anomalous product, 14b.](image-url)
Crystal structure determinations. Data on all the compounds were collected with a Nonius kappaCCD diffractometer; cell refinement and data reduction were done using SCALEPACK and DENZO-SMN [2]. Structure solution and refinement were carried out using the SHELXS97 and SHELXL97 program, respectively [3]. Parameters in CIF format are available as electronic supplementary information.

References:

