Cyclizations of *N*-Stannylaminyll Radicals onto Nitriles

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SUPPORTING INFORMATION

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General Procedures. All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 or 400 MHz (75 or 100 MHz for ^{13}C) in deuteriochloroform, unless otherwise stated, using tetramethylsilane as the internal standard. Mass spectra were determined by the electron impact method (EI, 70 eV) or electron spray ionization (ESI). IR spectra were recorded in chloroform. Column chromatography was carried out on ICN silica gel (70-230 or 230-400 mesh) by gradual elution with mixtures of light petroleum (bp 40-70 °C) and diethyl ether or dichloromethane or methanol and final elution with methanol. Previously reported reaction products were identified by spectral comparison. TBAB is tetrabutylammonium bromide. 2-Bromomethylbenzonitrile¹ and 2-azidomethylbenzonitrile (2)² were prepared according to the literature.

Monoalkylated malononitriles. These compounds were synthesized in 70-98% yield from malononitrile, alkyl halide, TBAB, and potassium carbonate (or potassium *tert*-butoxide) according to the procedure of Diez-Barra.³ 2-Ethylmalononitrile,³ 2-benzylmalononitrile,³ 2-allylmalononitrile,³ 2-[(*E*)-2-butenyl]-malononitrile,⁴ 2-(3-methyl-2-butenyl)malononitrile,⁵ and 2-[(*E*)-3-phenyl-2-propenyl]malononitrile⁶ are known compounds.

2-[(*Z*)-3-Hexenyl]malononitrile. Yield = 80%; oil; IR ν_{max} (cm^{-1}) 2258 (CN); ^1H NMR (400 MHz) δ 0.99 (3 H, t, J = 7.6 Hz), 2.07-2.14 (4 H, m), 2.39 (2 H, q, J = 7.6 Hz), 3.73 (1 H, t, J = 7.4 Hz), 5.19-5.27 (1 H, m), 5.56-5.64 (1 H, m); ^{13}C NMR (100 MHz) δ 14.79 (CH_3), 21.33 (CH_2), 22.24 (CH), 24.52 (CH_2), 31.51 (CH_2), 113.24 (CN), 124.34 (CH), 137.04 (CH); MS (ESI) 147 ($\text{M} - 1$)⁻.

Dialkylated malononitriles. These compounds were obtained in 30-75% yield from the corresponding monoalkylated malononitriles, 1,2-dibromoethane or 1,3-dibromopropane, TBAB, and potassium *tert*-butoxide again according to the above procedure.³

2-(2-Bromoethyl)-2-ethylmalononitrile. Yield = 40%; oil; IR ν_{max} (cm^{-1}) 2249 (CN); ^1H NMR (200 MHz) δ 1.31 (3 H, t, J = 7.7 Hz), 2.06 (2 H, q, J = 7.7 Hz), 2.49 (2 H, br t, J = 8.6 Hz), 3.59 (2 H, br t, J

= 8.6 Hz); ^{13}C NMR (50 MHz) δ 10.38 (CH_3), 24.88 (CH_2), 32.30 (CH_2), 38.74 (C), 40.18 (CH_2), 115.01 (CN); MS (EI) m/z (rel inten) 202 ($\text{M}^+ + 2$, 1), 200 (M^+ , 2), 107 (98), 79 (100).

2-(2-Bromoethyl)-2-benzylmalononitrile. Yield = 46%; mp = 97-98 °C; IR ν_{max} (cm^{-1}) 2249 (CN); ^1H NMR (300 MHz) δ 2.35 (2 H, t, $J = 8.2$ Hz), 3.11 (2 H, s), 3.45 (2 H, t, $J = 8.2$ Hz), 7.22-7.38 (5 H, m); ^{13}C NMR (75 MHz) δ 20.76 (CH_2), 35.09 (C), 35.95 (CH_2), 39.71 (CH_2), 110.67 (CN), 125.49 (CH), 125.54 (CH), 126.65 (CH), 127.70 (C); MS (EI) m/z (rel inten) 264 ($\text{M}^+ + 2$, 4), 262 (M^+ , 3), 91 (100); MS (ESI) 263 $[(\text{M} + 2) - 1]^-$, 261 ($\text{M} - 1$) $^-$.

2-Allyl-2-(2-bromoethyl)malononitrile. Yield = 50%; oil; IR ν_{max} (cm^{-1}) 2249 (CN); ^1H NMR (200 MHz) δ 2.48 (2 H, dd, $J_1 = 9.6$ Hz, $J_2 = 6.8$ Hz), 2.74 (2 H, dt, $J_d = 7.1$ Hz, $J_t = 1.0$ Hz), 3.53-3.67 (2 H, m), 5.38-5.52 (2 H, m), 5.78-6.00 (1 H, m); ^{13}C NMR (50 MHz) δ 24.77 (CH_2), 37.46 (C), 39.73 (CH_2), 42.14 (CH_2), 114.71 (CN), 124.53 (CH_2), 128.39 (CH); MS (ESI) 213 $[(\text{M} + 2) - 1]^-$, 211 ($\text{M} - 1$) $^-$.

2-(2-Bromoethyl)-2-[(E)-2-butenyl]malononitrile. Yield = 45%; oil; IR ν_{max} (cm^{-1}) 2250 (CN); ^1H NMR (300 MHz) δ 1.79 (3 H, d, $J = 7.2$ Hz), 2.46 (2 H, m), 2.67 (2 H, d, $J = 7.2$ Hz), 3.56 (2 H, m), 5.44-5.60 (1 H, m), 5.77-5.92 (1 H, m); ^{13}C NMR (75 MHz) δ 18.43 (CH_3), 24.96 (CH_2), 39.28 (CH_2), 40.94 (CH_2), 114.79 (CN), 120.94 (CH), 135.47 (CH); MS (ESI) 251 $[(\text{M} + 2) + \text{Na}]^+$, 249 ($\text{M} + \text{Na}$) $^+$, 229 $[(\text{M} + 2) + 1]^+$, 227 ($\text{M} + 1$) $^+$.

2-(2-Bromoethyl)-2-(3-methyl-2-butenyl)malononitrile. Yield = 41%; oil; IR ν_{max} (cm^{-1}) 2249 (CN); ^1H NMR (300 MHz) δ 1.73 (3 H, d, $J = 1.1$ Hz), 1.83 (3 H, d, $J = 1.1$ Hz), 2.44-2.49 (2 H, m), 2.72 (2 H, d, $J = 7.7$ Hz), 3.54-3.61 (2 H, m), 5.27 (1 H, tq, $J_t = 7.7$ Hz, $J_q = 1.4$ Hz); ^{13}C NMR (75 MHz) δ 18.43 (CH_3), 24.38 (CH_2), 26.05 (CH_3), 36.44 (CH_2), 39.24 (CH_2), 113.88 (CH), 114.61 (CN), 141.59 (C); MS (ESI) 241 $[(\text{M} + 2) - 1]^-$, 239 ($\text{M} - 1$) $^-$, 265 $[(\text{M} + 2) + \text{Na}]^+$, 263 ($\text{M} + \text{Na}$) $^+$.

2-(2-Bromoethyl)-2-[(E)-3-phenyl-2-propenyl]malononitrile. Yield = 30%; mp = 62-64 °C; IR ν_{max} (cm^{-1}) 2250 (CN); ^1H NMR (200 MHz) δ 2.47 (2 H, t, $J = 7.8$ Hz), 2.84 (2 H, dd, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz), 3.57 (2 H, t, $J = 7.8$ Hz), 6.17 (1 H, m), 6.69 (1 H, br d, $J = 15.5$ Hz), 7.22-7.51 (5 H, m); ^{13}C NMR (50 MHz) δ 24.84 (CH_2), 37.85 (C), 39.74 (CH_2), 41.68 (CH_2), 114.83 (CN), 118.86 (CH), 127.33 (CH),

129.17 (CH), 136.00 (C), 138.98 (CH); MS (EI) m/z (rel inten) 290 ($M^+ + 2$, 6), 288 (M^+ , 8), 117 (100), 91 (15).

2-(3-Bromopropyl)-2-ethylmalononitrile. Yield = 30%; oil; IR $\nu_{\max}$ (cm^{-1}) 2241 (CN); ^1H NMR (200 MHz) δ 1.30 (3 H, t, $J = 7.5$ Hz), 1.96-2.34 (6 H, m), 3.50 (2 H, t, $J = 6.0$ Hz); ^{13}C NMR (50 MHz) δ 10.51 (CH_3), 29.05 (CH_2), 31.92 (CH_2), 32.24 (CH_2), 36.65 (CH_2), 38.71 (C), 115.80 (CN); MS (EI) m/z (rel inten) 216 ($M^+ + 2$, 2), 214 (M^+ , 2), 186 (59), 107 (100).

2-(3-Bromopropyl)-2-[(E)-2-butenyl]malononitrile. Yield = 74%; oil; IR $\nu_{\max}$ (cm^{-1}) 2249 (CN); ^1H NMR (200 MHz) δ 1.79 (3 H, br d, $J = 6.9$ Hz), 2.32-2.04 (4 H, m), 2.65 (2 H, d, $J = 7.7$ Hz), 3.49 (2 H, t, $J = 6.0$ Hz), 5.43-5.62 (1 H, m), 5.75-6.04 (1 H, m); ^{13}C NMR (50 MHz) δ 14.01 (CH_3), 18.71 (CH), 29.00 (CH_2), 31.89 (CH_2), 32.21 (CH_2), 36.21 (CH_2), 30.02 (C), 41.35 (CH_2), 115.75 (CN), 121.45 (CH), 135.48 (CH); MS (EI) m/z (rel inten) 242 ($M^+ + 2$, <1), 240 (M^+ , <1), 161 (10), 55 (100).

2-(3-Bromopropyl)-2-(3-methyl-2-butenyl)malononitrile. Yield = 75%; oil; IR $\nu_{\max}$ (cm^{-1}) 2248 (CN); ^1H NMR (300 MHz) δ 1.73 (3 H, d, $J = 1.1$ Hz), 1.82 (3 H, d, $J = 0.84$ Hz), 2.07-2.15 (2 H, m), 2.18-2.29 (2 H, m), 2.70 (2 H, d, $J = 7.7$ Hz), 3.49 (2 H, t, $J = 6.03$ Hz), 5.28 (1 H, t quint, $J_t = 7.7$ Hz, $J_q = 1.38$ Hz); ^{13}C NMR (75 MHz) δ 18.41 (CH_3), 26.03 (CH), 28.49 (CH_2), 31.42 (CH_2), 35.56 (CH_2), 36.25 (CH_2), 37.32 (C), 114.38 (CH), 115.38 (C), 140.91 (CN); MS (ESI) 279 $[(M + 2) + \text{Na}]^+$, 277 $(M + \text{Na})^+$, 257 $[(M + 2) + 1]^+$, 255 $(M + 1)^+$.

2-(3-Bromopropyl)-2-[(E)-3-phenyl-2-propenyl]malononitrile. Yield = 30%; mp = 60-62 °C; IR $\nu_{\max}$ (cm^{-1}) 2251 (CN); ^1H NMR (200 MHz) δ 2.04-2.37 (4 H, m), 2.85 (2 H, br d, $J = 8.0$ Hz), 3.45 (2 H, t, $J = 7.0$ Hz), 6.20 (1 H, dt, $J_d = 15.6$ Hz, $J_t = 8.0$ Hz), 6.71 (1 H, br d, $J = 15.6$ Hz), 7.23-7.59 (5 H, m); ^{13}C NMR (50 MHz) δ 28.99 (CH_2), 31.82 (CH_2), 36.20 (CH_2), 37.87 (C), 41.54 (CH_2), 115.57 (CN), 119.40 (CH), 127.31 (CH), 129.15 (CH), 129.32 (CH), 136.18 (C), 138.58 (CH); MS (EI) m/z (rel inten) 304 ($M^+ + 2$, 5), 302 (M^+ , 6), 117 (100), 91 (13).

2-(2-Bromoethyl)-2-[(Z)-3-hexenyl]malononitrile. Yield = 59%; oil; IR $\nu_{\max}$ (cm^{-1}) 2249 (CN); ^1H NMR (300 MHz) δ 1.00 (3 H, t, $J = 7.4$ Hz), 1.98-2.14 (4 H, m), 2.35-2.53 (4 H, m), 3.55-3.61 (2 H, m),

5.26-5.35 (1 H, m), 5.50-5.58 (1 H, m); ^{13}C NMR (75 MHz) δ 14.65 (CH_3), 21.19 (CH_2), 23.89 (CH_2), 24.72 (CH_2), 37.51 (C), 38.18 (CH_2), 40.61 (CH_2), 114.99 (CN), 124.62 (CH), 135.71 (CH); MS (ESI) 255 $[(\text{M} + 2) - 1]^-$, 253 $(\text{M} - 1)^-$.

Azidated malononitriles. These compounds were obtained in 74-96% yield from the corresponding (bromoalkyl)malononitriles and sodium azide in dimethylsulfoxide and were purified by column chromatography.

2-(2-Azidoethyl)-2-ethylmalononitrile (1a). Yield = 98%; oil; IR ν_{max} (cm^{-1}) 2248 (CN) and 2106 (N_3); ^1H NMR (200 MHz) δ 1.27 (3 H, t, $J = 7.1$ Hz), 2.04 (2 H, q, $J = 7.1$ Hz), 2.18 (2 H, t, $J = 6.9$ Hz), 3.65 (2 H, t, $J = 6.9$ Hz); ^{13}C NMR (50 MHz) δ 9.91 (CH_3), 31.88 (CH_2), 35.93 (CH_2), 36.63 (C), 47.40 (CH_2), 115.08 (CN); MS (EI) m/z (rel inten) 135 ($\text{M}^+ - 28$, 17), 106 (34), 93 (25), 66 (49), 54 (100), 42 (99).

2-(2-Azidoethyl)-2-benzylmalononitrile (1b). Yield = 91%; mp = 42-43 °C; IR ν_{max} (cm^{-1}) 2241 (CN) and 2098 (N_3); ^1H NMR (300 MHz) δ 2.17 (2 H, t, $J = 7.0$ Hz), 3.24 (2 H, s), 3.67 (2 H, t, $J = 7.0$ Hz), 7.32-7.43 (5 H, m); ^{13}C NMR (75 MHz) δ 36.59 (CH_2), 37.50 (C), 44.16 (CH_2), 47.89 (CH_2), 115.07 (CN), 129.68 (CH), 130.89 (CH), 131.99 (C); MS (EI) m/z (rel inten) 225 (M^+ , <1), 197 (3), 118 (43), 91 (100).

2-Allyl-2-(2-azidoethyl)malononitrile (6a). Yield = 96%; oil; IR ν_{max} (cm^{-1}) 2241 (CN) and 2104 (N_3); ^1H NMR (200 MHz) δ 1.18 (2 H, t, $J = 7.1$ Hz), 2.75 (2 H, d, $J = 7.3$ Hz), 3.70 (2 H, t, $J = 7.1$ Hz), 5.36-5.56 (2 H, m), 5.77-6.03 (1 H, m); ^{13}C NMR (50 MHz) δ 35.82 (C), 36.23 (CH_2), 42.44 (CH_2), 47.78 (CH_2), 115.00 (CN), 124.47 (CH_2), 128.63 (CH); MS (EI) m/z (rel inten) 175 (M^+ , <1), 119 (3), 92 (7), 39 (54), 41 (100).

2-(2-Azidoethyl)-2-[(E)-2-butenyl]malononitrile (6b). Yield = 76%; oil; IR ν_{max} (cm^{-1}) 2254 (CN) and 2107 (N_3); ^1H NMR (300 MHz) δ 1.79 (3 H, br d, $J = 6.4$ Hz), 2.17 (2 H, t, $J = 7.0$ Hz), 2.68 (2 H, dt, $J_d = 7.1$ Hz, $J_t = 0.9$ Hz), 3.69 (2 H, t, $J = 7.0$ Hz), 5.47-5.59 (1 H, m), 5.71-6.03 (1 H, m); ^{13}C NMR

(75 MHz) δ 18.77 (CH₃), 35.96 (C), 36.30 (CH₂), 41.77 (CH₂), 47.92 (CH₂), 115.23 (CN), 121.22 (CH), 135.99 (CH); MS (EI) m/z (rel inten) 161 ($M^+ - 28$, 3), 135 (8), 92 (11), 39 (100).

2-(2-Azidoethyl)-2-(3-methyl-2-butenyl)malononitrile (6c). Yield = 90%; oil; IR $\nu_{\max}$ (cm⁻¹) 2249 (CN) and 2106 (N₃); ¹H NMR (300 MHz) δ 1.73 (3 H, br d, $J = 1.1$ Hz), 1.83 (3 H, br d, $J = 0.8$ Hz), 2.17 (2 H, t, $J = 7.2$ Hz), 2.73 (2 H, d, $J = 7.7$ Hz), 3.68 (2 H, t, $J = 7.1$ Hz), 5.28 (1 H, t quint, $J_t = 7.7$ Hz, $J_q = 1.4$ Hz); ¹³C NMR (75 MHz) δ 18.31 (CH₃), 25.91 (CH), 35.46 (CH₂), 36.54 (CH₂), 47.22 (CH₂), 113.96 (CH), 114.73 (CN), 141.31 (C); MS (ESI) 226 ($M + Na$)⁺.

2-(2-Azidoethyl)-2-[(E)-3-phenyl-2-propenyl]malononitrile (6d). Yield = 80%; mp = 26-27 °C; IR $\nu_{\max}$ (cm⁻¹) 2249 (CN) and 2094 (N₃); ¹H NMR (200 MHz) δ 2.14 (2 H, t, $J = 7.2$ Hz), 2.85 (2 H, br d, $J = 8.0$ Hz), 3.64 (2 H, t, $J = 7.2$ Hz), 6.19 (1 H, dt, $J_d = 15.2$ Hz, $J_t = 8.0$ Hz), 6.69 (1 H, br d, $J = 15.2$ Hz), 7.21-7.53 (5 H, m); ¹³C NMR (50 MHz) δ 36.02 (CH₂), 41.72 (CH₂), 47.68 (CH₂), 115.04 (CN), 119.11 (CH), 127.24 (CH), 129.13 (CH), 129.26 (CH), 136.03 (C), 138.73 (CH); MS (EI) m/z (rel inten) 251 (M^+ , 2), 223 ($M^+ - 28$, 18), 222 (61), 117 (100), 91 (30).

2-(2-Azidopropyl)-2-ethylmalononitrile (1c). Yield = 85%; oil; IR $\nu_{\max}$ (cm⁻¹) 2247 (CN) and 2102 (N₃); ¹H NMR (200 MHz) δ 1.30 (3 H, t, $J = 7.5$ Hz), 1.85-2.12 (6 H, m), 3.47 (2 H, t, $J = 6.0$ Hz); ¹³C NMR (50 MHz) δ 10.44 (CH₃), 25.89 (CH₂), 32.17 (CH₂), 35.21 (CH₂), 38.94 (C), 50.73 (CH₂), 115.79 (CN); MS (EI) m/z (rel inten) 162 ($M^+ - 15$, 2), 149 ($M^+ - 28$, 5), 121 (5), 107 (6), 93 (29), 79 (100), 42 (92).

2-(3-Azidopropyl)-2-[(E)-2-butenyl]malononitrile (7a). Yield = 74%; oil; IR $\nu_{\max}$ (cm⁻¹) 2249 (CN) and 2100 (N₃); ¹H NMR (300 MHz) δ 1.78 (3 H, br d, $J = 6.6$ Hz), 1.87-2.05 (4 H, m), 2.59 (2 H, br dd, $J_t = 7.4$ Hz, $J_2 = 0.8$ Hz), 3.44 (2 H, m), 5.46-5.56 (1 H, m), 5.78-5.89 (1 H, m); ¹³C NMR (75 MHz) δ 13.74 (CH₃), 18.46 (CH), 25.64 (CH₂), 45.50 (CH₂), 38.07 (C), 41.03 (CH₂), 50.55 (CH₂), 115.61 (CN), 121.38 (CH), 135.10 (CH); MS (EI) m/z (rel inten) 188 ($M^+ - 15$, <1), 55 (100).

2-(3-Azidopropyl)-2-(3-methyl-2-butenyl)malononitrile (7b). Yield = 86%; oil; IR $\nu_{\max}$ (cm⁻¹) 2248 (CN) and 2101 (N₃); ¹H NMR (400 MHz) δ 1.73 (3 H, d, $J = 0.9$ Hz), 1.83 (3 H, d, $J = 0.9$ Hz),

1.99 (4 H, m), 2.69 (2 H, d, $J = 7.7$ Hz), 3.46 (2 H, t, $J = 6.0$ Hz), 5.28 (1 H, t quint, $J_t = 7.7$ Hz, $J_q = 1.4$ Hz); ^{13}C NMR (100 MHz) δ 19.04 (CH_3), 26.03 (CH_2), 26.67 (CH_3), 34.97 (CH_2), 37.05 (CH_2), 38.23 (C), 50.82 (CH_2), 114.96 (CH), 116.01 (CN), 141.67 (C); MS (ESI) 240 ($\text{M} + \text{Na}$) $^+$, 218 ($\text{M} + 1$) $^+$.

2-(3-Azidopropyl)-2-[(E)-3-phenyl-2-propenyl]malononitrile (7c). Yield = 82%; mp = 27-28 °C; IR ν_{max} (cm^{-1}) 2249 (CN) and 2097 (N_3); ^1H NMR (200 MHz) δ 1.81-2.12 (4 H, m), 2.83 (2 H, dd, $J_t = 8.0$ Hz, $J_2 = 1.2$ Hz), 3.40 (2 H, t, $J = 7.0$ Hz), 6.19 (1H, d t, $J_d = 15.2$ Hz, $J_t = 8.0$ Hz), 6.68 (1 H, br d, $J = 15.2$ Hz), 7.23-7.54 (5 H, m); ^{13}C NMR (50 MHz) δ 25.78 (CH_2), 34.76 (CH_2), 38.06 (C), 41.49 (CH_2), 50.57 (CH_2), 115.54 (CN), 119.40 (CH), 127.16 (CH), 127.25 (CH), 129.08 (CH), 129.27 (CH), 136.14 (C), 138.44 (CH); MS (EI) m/z (rel inten) 265 (M^+ , <1), 237 ($\text{M}^+ - 28$, 14) 236 (43), 158 (44), 117 (81), 115 (100), 91 (71).

2-(2-Azidoethyl)-2-[(Z)-3-hexenyl]malononitrile (8). Yield = 80%; oil; IR ν_{max} (cm^{-1}) 2249 (CN) and 2105 (N_3); ^1H NMR (300 MHz) δ 1.00 (3 H, t, $J = 7.4$ Hz), 1.92-2.15 (4 H, m), 2.21 (2 H, t, $J = 7.1$ Hz), 2.32-2.50 (2 H, m), 3.70 (2 H, t, $J = 7.1$ Hz), 5.26-5.36 (1 H, m), 5.48-5.59 (1 H, m); ^{13}C NMR (75 MHz) δ 14.75 (CH_3), 21.30 (CH_2), 24.04 (CH_2), 35.90 (C), 37.24 (CH_2), 38.59 (CH_2), 47.85 (CH_2), 115.29 (CN), 124.78 (CH), 135.80 (CH); MS (ESI) 240 ($\text{M} + \text{Na}$) $^+$.

General Procedure for the Reactions of Azidomalononitriles with Tributyltin Hydride. A benzene (15 mL) solution of tributyltin hydride (5.5 mmol) and AIBN (0.5 mmol) was added by a syringe pump in 3 h to a refluxing benzene (100 mL) solution of azidomalononitrile (5 mmol). The resulting mixture was refluxed for an additional hour. The solvent was then removed and the residue was chromatographed on silica gel; addition of methanol to the eluant was always necessary to elute the reaction product(s). In some cases (**6c**, **7a**), most of the main product precipitated by concentration of the mixture and addition of a small amount of acetone; the solid was collected by filtration and the filtrate was chromatographed to obtain a further amount of product: the reported yields refer to the whole isolated quantity. In two cases (**1b,c**), column chromatography was followed by a destannylation

procedure⁷ and finally by a further chromatography. All the azides were recovered completely unchanged after a 4-h reflux in benzene solution in the absence of stannane and AIBN. The yields of the main reaction products are reported in Table 1; physical and spectroscopic characterizations are described below.

3-Ethyl-2-imino-3-pyrrolidinecarbonitrile (3a). mp = 93-95 °C; IR $\nu_{\max}$ (cm⁻¹) 3404 (NH), 2234 (CN) and 1664 (C=N); ¹H NMR (200 MHz) δ 1.13 (3 H, t, J = 7.3 Hz), 1.62-1.81 (1 H, m), 1.86-2.05 (1 H, m), 2.15 (1 H, ddd, J_1 = 13.0 Hz, J_2 = 7.2 Hz, J_3 = 4.2 Hz), 2.45 (1 H, ddd, J_1 = 13.0 Hz, J_2 = 8.5 Hz, J_3 = 7.2 Hz), 3.48-3.76 (2 H, m), 5.56 (2 H, br s, NH); ¹³C NMR (50 MHz) δ 10.27 (CH₃), 29.45 (CH₂), 35.92 (CH₂), 49.47 (C), 53.38 (CH₂), 121.30 (CN), 163.63 (C=N); MS (EI) m/z (rel inten) 137 (M⁺, 46), 122 (11), 108 (11), 56 (100). Anal. calcd for C₇H₁₁N₃: C, 61.29; H, 8.08; N, 30.63. Found: C, 61.40; H, 8.09; N, 30.51.

3-Benzyl-2-imino-3-pyrrolidinecarbonitrile (3b). mp = 160-161 °C; IR $\nu_{\max}$ (cm⁻¹) 3400 (NH), 2234 (CN) and 1664 (C=N); ¹H NMR (300 MHz) δ 2.22-2.43 (2 H, m), 3.00 (1 H, A part of AB, J = 13.7 Hz), 3.13 (1 H, B part of AB, J = 13.7 Hz), 3.28-3.37 (1 H, m), 3.63 (1 H, ddd, J_1 = 11.4 Hz, J_2 = 8.3 Hz, J_3 = 3.0 Hz), 4.85 (2 H, br s, NH), 7.31-7.39 (5 H, m); ¹³C NMR (75 MHz) δ 36.53 (CH₂), 41.82 (CH₂), 49.83 (C), 53.56 (CH₂), 121.35 (CN), 128.56 (CH), 129.34 (CH), 130.70 (CH), 135.00 (C), 162.89 (C=N); MS (EI) m/z (rel inten) 199 (M⁺, 8), 91 (100). Anal. calcd for C₁₂H₁₃N₃: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.28; H, 6.59; N, 21.13.

3-Ethyl-2-oxo-3-piperidinecarbonitrile (4). mp = 94-96 °C; IR $\nu_{\max}$ (cm⁻¹) 3396 (NH), 2234 (CN) and 1675 (C=O); ¹H NMR (300 MHz) δ 1.11 (3 H, t, J = 7.5 Hz), 1.80-2.30 (6 H, m), 3.25-3.48 (2 H, m), 7.12 (1 H, br s, NH); ¹³C NMR (75 MHz) δ 9.63 (CH₃), 19.75 (CH₂), 30.19 (CH₂), 30.70 (CH₂), 42.82 (CH₂), 45.01 (C), 121.18 (CN), 168.03 (C=O); MS (EI) m/z (rel inten) 152 (M⁺, 5), 137 (27), 124 (100), 82 (93). Anal. calcd for C₈H₁₂N₂O: C, 63.13; H, 7.95; N, 18.41. Found: C, 63.02; H, 7.94; N, 18.50.

1-Isoindolinimine (5).⁸ IR $\nu_{\max}$ (cm⁻¹) 3417 (NH), 3326 (NH) and 1637 (C=N); ¹H NMR (200 MHz) δ 3.80 (2 H, br s), 4.70 (2 H, s), 7.38-8.00 (3 H, m), 8.15 (1 H, d, J = 8.5 Hz); MS (EI) m/z (rel inten) 132 (M⁺, 88), 104 (100), 77 (54). Anal. calcd for C₈H₈N₂: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.77; H, 6.12; N, 21.11.

3-Allyl-2-imino-3-pyrrolidinecarbonitrile (9a). IR $\nu_{\max}$ (cm⁻¹) 3402 (NH), 2236 (CN) and 1675 (C=N); MS (EI) m/z (rel inten) 149 (M⁺, 34), 108 (20), 41 (100). No reliable NMR spectra could be obtained due to product insolubility. Anal. calcd for C₈H₁₁N₃: C, 64.40; H, 7.43; N, 28.16. Found: C, 64.53; H, 7.40; N, 28.07.

5-Ethyl-2,3,4,5-tetrahydropyrrolo[2,3-*b*]pyrrolo-3a(1*H*)-carbonitrile (10b). mp = 147.5-149.4 °C; IR $\nu_{\max}$ (cm⁻¹) 3451 (NH), 2236 (CN) and 1690 (C=N); ¹H NMR (300 MHz) δ 0.98 (3 H, t, J = 7.4 Hz), 1.45-1.77 (3 H, m), 1.98 (1 H, ddd, J_1 = 12.4 Hz, J_2 = 10.4 Hz, J_3 = 8.0 Hz), 2.46 (1 H, dd, J_1 = 12.4 Hz, J_2 = 4.8 Hz), 2.56 (1 H, dd, J_1 = 12.4 Hz, J_2 = 4.7 Hz), 3.83 (1 H, dd, J_1 = 11.8 Hz, J_2 = 7.9 Hz), 4.01 (1 H, td, J_t = 10.9 Hz, J_d = 5.0 Hz), 4.24 (1 H, m), 5.76 (1 H, br s, NH); ¹³C NMR (75 MHz) δ 10.64 (CH₃), 29.11 (CH₂), 36.41 (CH₂), 42.38 (CH₂), 49.54 (C), 54.90 (CH₂), 69.79 (CH), 119.42 (CN), 170.17 (C=N); MS (EI) m/z (rel inten) 163 (M⁺, 43), 148 (8), 134 (100). Anal. calcd for C₉H₁₃N₃: C, 66.23; H, 8.03; N, 25.74. Found: C, 66.15; H, 8.06; N, 25.79.

5-Isopropyl-2,3,4,5-tetrahydropyrrolo[2,3-*b*]pyrrolo-3a(1*H*)-carbonitrile (10c). IR $\nu_{\max}$ (cm⁻¹) 3453 (NH), 2236 (CN) and 1690 (C=N); ¹H NMR (300 MHz) δ 0.90 (3 H, d, J = 6.6 Hz), 1.02 (3 H, d, J = 6.6 Hz), 1.56 (1 H, dd, J_1 = 12.4 Hz, J_2 = 10.2 Hz), 1.69 (1 H, sext, J = 6.6 Hz), 1.97 (1 H, ddd, J_1 = 12.4 Hz, J_2 = 10.4 Hz, J_3 = 8.0 Hz), 2.47 (1 H, dd, J_1 = 12.4 Hz, J_2 = 5.0 Hz), 2.52 (1 H, dd, J_1 = 12.4 Hz, J_2 = 4.7 Hz), 3.84 (1 H, dd, J_1 = 12.1 Hz, J_2 = 8.0 Hz), 3.95-4.09 (2 H, m), 6.70 (1 H, br s, NH); ¹³C NMR (100 MHz) δ 18.46 (CH₃), 20.01 (CH₃), 35.58 (CH), 36.46 (CH₂), 40.54 (CH₂), 49.51 (C), 55.14 (CH₂), 74.45 (CH), 119.48 (CN), 170.05 (C=N); MS (ESI) 178 (M + 1)⁺, 176 (M - 1)⁻. Anal. calcd for C₁₀H₁₅N₃: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.87; H, 8.51; N, 23.62.

5-Benzyl-2,3,4,5-tetrahydropyrrolo[2,3-*b*]pyrrolo-3a-(1*H*)-carbonitrile (10d). mp = 223-225 °C (from ethanol); IR $\nu_{\max}$ (cm⁻¹) 3448 (NH), 2236 (CN) and 1689 (C=N); ¹H NMR (300 MHz) δ 1.59 (1 H, dd, $J_1 = 12.7$ Hz, $J_2 = 10.0$ Hz), 1.87-2.03 (1 H, m), 2.48 (2 H, ddd, $J_1 = 14.5$ Hz, $J_2 = 12.7$ Hz, $J_3 = 4.5$ Hz), 2.74-2.95 (2 H, m), 3.61 (1 H, dd, $J_1 = 11.8$ Hz, $J_2 = 8.2$ Hz), 3.79-3.93 (1 H, m), 4.54-4.69 (1 H, m), 6.40 (1 H, br s, NH), 7.15-7.39 (5 H, m); ¹³C NMR (75 MHz) δ 36.72 (CH₂), 43.32 (CH₂), 43.53 (CH₂), 50.17 (C), 53.82 (CH₂), 71.43 (CH), 119.96 (CN), 127.23 (CH), 129.22 (CH), 129.28 (CH), 138.86 (C), 170.77 (C=N); MS (EI) m/z (rel inten) 225 (M⁺, 4), 134 (100), 91 (12). The structure of **10d** was also confirmed by X-ray diffraction (see below). Anal. calcd for C₁₄H₁₅N₃: C, 76.64; H, 6.71; N, 18.65. Found: C, 74.69; H, 6.74; N, 18.57.

2-Ethyl-2,3,4,5,6,7-hexahydro-3a*H*-pyrrolo[2,3-*b*]pyridino-3a-carbonitrile (11a). mp = 170-171.5 °C; IR $\nu_{\max}$ (cm⁻¹) 3451 (NH), 2225 (CN) and 1665 (C=N); ¹H NMR (300 MHz) δ 1.00 (3 H, t, $J = 7.4$ Hz), 1.32-1.52 (2 H, m), 1.56 (1 H, dd, $J_1 = 13.2$ Hz, $J_2 = 3.3$ Hz), 1.63-1.77 (1 H, m), 1.85-1.94 (1 H, m), 2.05-2.21 (1 H, m), 2.41 (1 H, dt, $J_d = 13.2$ Hz, $J_t = 3.3$ Hz), 2.60 (1 H, dd, $J_1 = 12.4$ Hz, $J_2 = 5.0$ Hz), 3.14 (1 H, td, $J_t = 11.8$ Hz, $J_d = 4.4$ Hz), 3.36 (1 H, dd, $J_1 = 11.8$ Hz, $J_2 = 5.0$ Hz), 3.68-3.77 (1 H, m), 6.16 (1 H, br s, NH); ¹³C NMR (100 MHz) δ 11.66 (CH₃), 21.29 (CH₂), 29.92 (CH₂), 33.33 (CH₂), 43.38 (CH₂), 44.22 (CH₂), 44.68 (C), 65.53 (CH), 121.13 (CN), 161.61 (C=N); MS (ESI) 178 (M + 1)⁺. Anal. calcd for C₁₀H₁₅N₃: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.74; H, 8.51; N, 23.75.

2-Isopropyl-2,3,4,5,6,7-hexahydro-3a*H*-pyrrolo[2,3-*b*]pyridino-3a-carbonitrile (11b). mp = 172-174 °C; IR $\nu_{\max}$ (cm⁻¹) 3397 (NH), 2235 (CN) and 1653 (C=N); ¹H NMR (400 MHz) δ 0.90 (3 H, d, $J = 6.7$ Hz), 1.06 (3 H, d, $J = 6.7$ Hz), 1.47 (1 H, dd, $J_1 = 12.5$ Hz, $J_2 = 9.8$ Hz), 1.53 (1 H, td, $J_t = 13.2$ Hz, $J_d = 3.3$ Hz), 1.63 (1 H, m), 1.85-1.94 (1 H, m), 2.07-2.21 (1 H, m), 2.42 (1 H, dt, $J_d = 13.2$ Hz, $J_t = 3.3$ Hz), 2.55 (1 H, dd, $J_1 = 12.3$ Hz, $J_2 = 5.1$ Hz), 3.15 (1 H, td, $J_t = 11.8$ Hz, $J_d = 4.2$ Hz), 3.39 (1 H, dddd, $J_1 = 11.7$ Hz, $J_2 = 5.5$ Hz, $J_3 = 2.0$ Hz, $J_4 = 1.1$ Hz), 3.53 (1 H, ddd, $J_1 = 13.0$ Hz, $J_2 = 7.9$ Hz, $J_3 = 5.1$ Hz), 5.00 (1 H, br s, NH); ¹³C NMR (100 MHz) δ 19.36 (CH₃), 20.96 (CH₃), 21.31 (CH₂), 33.58 (CH₂), 34.07 (CH), 42.15 (CH₂), 43.83 (CH₂), 44.59 (C), 70.06 (CH), 120.95 (CN), 161.41 (C=N); MS (ESI)

192 ($M + 1$)⁺. Anal. calcd for C₁₁H₁₇N₃: C, 69.07; H, 8.96; N, 21.97. Found: C, 68.95; H, 8.99; N, 22.06.

2-Benzyl-2,3,4,5,6,7-hexahydro-3aH-pyrrolo[2,3-*b*]pyridino-3a-carbonitrile (11c). mp = 198-199 °C (from ethyl acetate); IR $\nu_{\max}$ (cm⁻¹) 3391 (NH), 2232 (CN) and 1648 (C=N); ¹H NMR (300 MHz) δ 1.40-1.58 (2 H, m), 1.78-1.92 (1 H, m), 1.98-2.17 (1 H, m), 2.35 (1 H, dt, $J_d = 12.7$ Hz, $J_t = 1.0$ Hz), 2.46 (1 H, dd, $J_t = 12.7$ Hz, $J_2 = 5.1$ Hz), 2.64 (1 H, dd, $J_t = 14.0$ Hz, $J_2 = 7.7$ Hz), 2.98-3.23 (3 H, m), 4.03-4.17 (1 H, m), 6.38 (1 H, br s, NH), 7.15-7.38 (5 H, m); ¹³C NMR (75 MHz) δ 21.19 (CH₂), 33.21 (CH₂), 43.08 (CH₂), 43.36 (CH₂), 44.36 (CH₂), 44.64 (C), 65.22 (CH), 120.92 (CN), 126.95 (CH), 129.07 (CH), 129.59 (CH), 139.36 (C), 162.00 (C=N); MS (EI) m/z (rel inten) 148 ($M^+ - 91$, 100), 120 (13), 91 (8). The structure of **11c** was also confirmed by X-ray diffraction (see below). Anal. calcd for C₁₅H₁₇N₃: C, 75.28; H, 7.16; N, 17.56. Found: C, 75.38; H, 7.13; N, 17.49.

From this reaction a small amount (<5%) of the mono-cyclized product **2-oxo-3-[(*E*)-3-phenyl-2-propenyl]-3-piperidinecarbonitrile** was also obtained; mp = 113-115 °C; IR $\nu_{\max}$ (cm⁻¹) 3401 (NH), 2233 (CN) and 1679 (C=O); ¹H NMR (300 MHz) δ 1.91-2.08 (3 H, m), 2.17-2.27 (1 H, m), 2.78-2.85 (1 H, m), 3.00-3.07 (1 H, m), 3.29-3.48 (2 H, m), 6.19 (1 H, dt, $J_d = 15.1$ Hz, $J_t = 7.5$ Hz), 6.57 (1 H, br d, $J = 15.1$ Hz), 6.68 (1 H, br s, NH), 7.25-7.40 (5 H, m); ¹³C NMR (75 MHz) δ 19.85 (CH₂), 30.38 (C), 31.04 (CH₂), 40.41 (CH₂), 43.00 (CH₂), 120.94 (CN), 122.85 (CH), 127.09 (CH), 128.58 (CH), 129.29 (CH), 136.47 (CH), 137.10 (C), 167.13 (CO); MS (EI) m/z (rel inten) 240 (M^+ , 31), 117 (100), 91 (35). Anal. calcd for C₁₅H₁₆N₂O: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.99; H, 6.70; N, 11.63.

3-[(*Z*)-3-Hexenyl]-2-imino-3-pyrrolidinecarbonitrile (16). IR $\nu_{\max}$ (cm⁻¹) 3406 (NH), 2237 (CN) and 1666 (C=N); ¹H NMR (400 MHz) δ 0.98 (3 H, t, $J = 7.5$ Hz), 1.63-1.76 (1 H, m), 1.80-1.96 (1 H, m), 1.98-2.13 (3 H, m), 2.14-2.26 (2 H, m), 2.45-2.53 (1 H, m), 3.55-3.65 (1 H, m), 3.72 (1 H, ddd, $J_t = 8.4$ Hz, $J_2 = 4.0$ Hz, $J_3 = 1.4$ Hz), 5.26-5.34 (1 H, m), 5.40-5.50 (1 H, m), 4.54-5.01 (2 H, br s, NH); ¹³C NMR (100 MHz) δ 14.86 (CH₃), 21.25 (CH₂), 24.00 (CH₂), 36.21 (CH₂), 36.75 (CH₂), 48.79 (C), 53.88

(CH₂), 121.19 (CN), 126.6 (CH), 134.58 (CH), 163.00 (C=N); MS (ESI) 192 (M + 1)⁺. Anal. calcd for C₁₁H₁₇N₃: C, 69.07; H, 8.96; N, 21.97. Found: C, 69.04; H, 8.97; N, 21.99.

From this reaction a small amount (<5%) of **5-((E)-2-{5-cyano-5-[(Z)-3-hexenyl]-2-pyrrolidinylidene}hydrazone)-2-[(Z)-3-hexenyl]-2-pyrrolidinecarbonitrile** (the probable dimer of compound **16**) was also obtained; MS (ESI) 403 (M + Na)⁺, 381 (M + 1)⁺.

2-Imino-3-(3-methyl-2-butenyl)-3-pyrrolidinecarbonitrile (9c). This compound was obtained by reacting azide **6c** with tributyltin hydride in the absence of AIBN; mp = 110.9-112.6 °C; IR $\nu_{\max}$ (cm⁻¹) 3405 (NH), 3501 (NH), 2238 (CN) and 1664 (C=N); ¹H NMR (300 MHz) δ 1.68 (3 H, d, *J* = 1.1 Hz), 1.78 (3 H, d, *J* = 0.8 Hz), 2.11-2.19 (1 H, ddd, *J*₁ = 13.0 Hz, *J*₂ = 7.2 Hz, *J*₃ = 3.9 Hz), 2.34-2.50 (2 H, dd, *J*₁ = 8.5 Hz, *J*₂ = 7.1 Hz), 2.58 (1 H, dd, *J*₁ = 14.6 Hz, *J*₂ = 7.7 Hz), 3.69 (1 H, ddd, *J*₁ = 13.6 Hz, *J*₂ = 8.5 Hz, *J*₃ = 3.9 Hz), 3.50-3.63 (1 H, m), 5.24 (1 H, t quint, *J*_t = 7.4 Hz, *J*_q = 1.4 Hz), 4.91 (2 H, br s, NH); ¹³C NMR (75 MHz) δ 18.11 (CH₃), 25.91 (CH₃), 34.11 (CH₂), 35.82 (CH₂), 48.00 (C), 52.93 (CH₂), 116.8 (CH), 55.14 (CH₂), 120.71 (CN), 138.08 (C), 162.60 (C=N); MS (ESI) 178 (M + 1)⁺. Anal. calcd for C₁₀H₁₅N₃: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.87; H, 8.51; N, 23.62. This compound proved to be perfectly stable when kept for several hours in a refluxing benzene solution in the presence of AIBN.

2-Imino-3-[(E)-3-phenyl-2-propenyl]-3-pyrrolidinecarbonitrile (9d). This compound was obtained by reacting azide **6d** with tributyltin hydride in the absence of AIBN; IR $\nu_{\max}$ (cm⁻¹) 3404 (NH), 2238 (CN) and 1665 (C=N); ¹H NMR (300 MHz) δ 2.18-2.32 (1 H, m), 2.39-2.54 (1 H, m), 2.55-2.69 (1 H, m), 2.70-2.82 (1 H, m), 3.50-3.77 (2 H, m), 4.78 (2 H, br s, NH), 6.20 (1 H, m), 6.60 (1 H, br d, *J* = 16.0 Hz), 7.16-7.48 (5 H, m); MS (EI) *m/z* (rel inten) 225 (M⁺, 12), 117 (100), 91 (51). Anal. calcd for C₁₄H₁₅N₃: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.59; H, 6.72; N, 18.69. This compound proved to be perfectly stable when kept for several hours in a refluxing benzene solution in the presence of AIBN.

Single crystal X-ray analyses

Crystallographic data were collected at 298 K on a Enraf-Nonius CAD4 diffractometer using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (SIR97⁹) and anisotropically refined for all the non-H atoms. The refinements were performed on F^2 using SHELX93.¹⁰ The hydrogen atoms were located from a difference Fourier map and isotropically refined with displacement parameter 1.2 greater than the U_{eq} of the attached atoms. The H atoms attached to the carbon atoms were refined using a riding model. In **10d** one hydrogen atom was found to be statistically distributed over two positions associated to the nitrogen atoms of the five-membered rings. During the refinement the site occupation factors were allowed to vary freely, converging to 0.65(3) and 0.35(3) for the positions associated to N1 and N2 respectively.

10d: C₁₄H₁₅N₃, $M_r = 225.3$, orthorhombic, space group $Pbca$, $a = 10.819(2)$, $b = 9.869(2)$, $c = 22.487(5)$ $\text{\AA}$, $V = 2401.0(8) \text{ \AA}^3$, $Z = 8$, $\rho_{calc} = 1.246 \text{ g cm}^{-3}$, $\mu = 0.596 \text{ mm}^{-1}$; colorless prism, crystal dimensions $0.18 \times 0.20 \times 0.28 \text{ mm}$, 161 parameters, $R = 0.047$, $wR2 = 0.091$ (for 1809 unique reflections, $I > 0$), $S = 0.938$, $\Delta\rho$ (min/max) = $-0.12/0.20 \text{ e \AA}^{-3}$

11c: C₁₅H₁₇N₃, $M_r = 239.3$, monoclinic, space group $P2_1/n$, $a = 7.504(2)$, $b = 15.354(4)$, $c = 11.812(4)$ $\text{\AA}$, $\beta = 105.48(3)^\circ$, $V = 1311.6(7) \text{ \AA}^3$, $Z = 4$, $\rho_{calc} = 1.212 \text{ g cm}^{-3}$, $\mu = 0.573 \text{ mm}^{-1}$; colorless prism, crystal dimensions $0.08 \times 0.13 \times 0.32 \text{ mm}$, 166 parameters, $R = 0.042$, $wR2 = 0.097$ (for 2203 unique reflections, $I > 0$), $S = 0.991$, $\Delta\rho$ (min/max) = $-0.17/0.03 \text{ e \AA}^{-3}$.

Figure 1. Single crystal X-ray structure of **10d** showing the labeling scheme adopted. Only one position for the disordered hydrogen atom associated to the nitrogen atoms of the five-membered rings is given.

Figure 2. Single crystal X-ray structure of **11c** showing the labeling scheme adopted.

Comment to the structures

Compound **10d**.

Both the five-membered rings assume a twist conformation.

Bond distances and angles are as expected. The values of the bond distances indicate the presence of partial double bond character for the N1-C6 (1.308(3) Å) and N2-C6 (1.299(3) Å) bonds. This reflects in the disorder observed for the associated hydrogen atom, which was found to be statistically attached to both nitrogen atoms with site occupation factors of 0.65(3) and 0.35(3) for the position related to N1 and N2, respectively.

As observed in **11c** (see below), in the packing centrosymmetric pairs of molecules interact through hydrogen bonds giving rise to dimers:

N1-H1N, 0.78 Å; H1N...N2', 2.20 Å; N1-H1N...N2', 161.4°

N2-H2N, 0.76 Å; H2N...N1', 2.25 Å; N1-H1N...N2', 154.2°

(a prime denotes a transformation of $-x, -y, -z$)

Compound **11c**.

The six- and five-membered rings assume a chair and twist conformation, respectively.

Bond distances and angles are as expected; the value of the N2-C7 bond distance (1.278(2) Å) is consistent with a localized double-bond character.

In the packing centrosymmetric pairs of molecules interact through hydrogen bonds resulting in the formation of dimers:

N1-H1N, 0.87 Å; H1N...N2', 2.12 Å; N1-H1N...N2', 175.4°

(a prime denotes a transformation of $-x, 1-y, -z$)

Beckwith-Houk transition state models for cyclization of aminoiminyl **12d** ($\text{SnBu}_3 = \text{Me}$):

Chair-like TS (axial CN) ($\rightarrow$ *trans*-bicyclic radical), favored

Boat-like TS ($\rightarrow$ *cis*-bicyclic radical), disfavored

Chair-like TS (equatorial CN), disfavored, the iminyl moiety is very distant from the $\text{C}=\text{C}$ double bond

Optimized (DFT) structures of radicals *cis*-**14b** and *trans*-**14b** (SnBu₃ = SnMe₃), respectively:

Structures were optimized with the DFT program included in the Wavefunction *PC Spartan Pro* 1.0.3 package. For sake of simplicity, the tributyltin group was replaced with a trimethyltin moiety. After a careful conformational search, the geometries of the open-shell intermediates were fully optimized following the pBP/DN^{**} parameterization. The energy minimum of *cis*-**14b** was located at –6659.75571 H and that of *trans*-**14b** at –6659.75747 H, corresponding to an energy difference of 1.1 kcal/mol in favor of the *trans*-radical. Both structures gave $\langle S \rangle^2$ values of 0.752.

Optimized (DFT) structures of 3-ethyl-2-imino-3-pyrrolidinecarbonitrile (**3a**), and tautomeric 5-amino-4-ethyl-3,4-dihydro-2*H*-pyrrole-4-carbonitrile, respectively:

Structures were optimized with the DFT program (pBP/DN^{**} parameterization) included in the Wavefunction *PC Spartan Pro* 1.0.3 package. The energy minimum of **3a** (left structure) was located at -437.76931 H and that of its tautomeric amine (right structure) at -437.77251 H, corresponding to an energy difference of 2.0 kcal/mol in favor of the latter.

References

- ¹ Fuson, R. C. *J. Am. Chem. Soc.* **1926**, 48, 830.
- ² L'Abbé, G.; Sannen, I.; Dehaen, W. *J. Chem. Soc., Perkin Trans. I* **1993**, 27.
- ³ Diez-Barra, E.; De La Hoz, A.; Moreno, A.; Sanchez-Verdù, P. *J. Chem. Soc., Perkin Trans. I* **1991**, 2589.
- ⁴ Curran, D. P.; Seong, C. M. *Tetrahedron* **1992**, 48, 2175.
- ⁵ Kolsaker, P.; Storesund, H. J.; Gulbrandsen, T.; Wøien, G. *Acta Chem. Scand.* **1983**, B 37, 187.
- ⁶ Giambastiani, G.; Poli, G. *J. Org. Chem.* **1998**, 63, 9608.
- ⁷ Kizil, M.; Patro, B.; Callaghan, O.; Murphy, J. A.; Hursthouse, M. B.; Hibbs, D. *J. Org. Chem.* **1999**, 64, 7856.
- ⁸ (a) Sawanishi, H.; Sashida, H.; Tsuchiya, T. *Chem. Pharm. Bull.* **1985**, 33, 4564. (b) Sieveking, H. U.; Luettker, W. *Angew. Chem. Int. Ed.* **1969**, 8, 457.
- ⁹ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.*, **1999**, 32, 115-119.
- ¹⁰ Sheldrick, G. M. SHELXL93. Program for crystal structure refinement. University of Göttingen, Germany, **1993**.