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tert-Amino-effect in naphthalene proton sponges: a novel approach to benzo[*h*]quinoline and quino[7,8:7',8']quinoline derivatives

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6d: was obtained as above in 4 ml of PhMe. After evaporation of the solvent, the oily cherry-coloured residue was treated with *n*-hexane (5 ml) to yield 0.076 g (78%) of **6d** as orange-red crystals with mp 60–62 °C. IR (ν/cm^{-1}): 2224, 2214 (C≡N), 1703 (C=O). ^{1}H NMR (CDCl$_3$) δ: 1.39 (t, 3H, CH$_3$, ^3J 7.0 Hz), 2.73 (s, 6H, 8-NMe$_2$), 3.17 (s, 6H, 1-NMe$_2$), 4.34 (q, 2H, OCH$_2$, ^3J 7.0 Hz), 7.02 (d, 1H, H-7, ^3J 6.6 Hz), 7.31–7.39 (m, 3H, H-3,5,6), 7.96 (d, 1H, H-4, ^3J 8.5 Hz), 8.46 (s, 1H, –CH=).

8a: A mixture of **5** (0.07 g, 0.29 mmol) and malonodinitrile (0.021 g, 0.32 mmol) in 7 ml EtOH was kept at room temperature for 48 h. Shiny colourless crystals of **8a** (0.055 g, 65%) were filtered off, washed with cold EtOH and dried in air, mp 157–158 °C (from *n*-hexane). IR (ν/cm^{-1}): 2245 (C≡N). ^{1}H NMR (CDCl$_3$) δ: 2.75 (br. s, 6H, 10-NMe$_2$), 3.08 (s, 3H, 1-NMe), 3.65 (s, 2H, 4-CH$_2$), 3.98 (br. s, 2H, 2-CH$_2$), 6.97 (m, 1H, H-9), 7.02 (d, 1H, H-5, ^3J 8.5 Hz), 7.28–7.35 (m, 2H, H-7,8), 7.39 (d, 1H, H-6, ^3J 8.2 Hz).

8b: A mixture of **5** (0.07 g, 0.29 mmol), dimedone (0.04 g, 0.29 mmol) and piperidine (0.025 g, 0.29 mmol) in PhMe (8 ml) was kept at room temperature for 24 h. Standard workup gave 0.10 g (96%) of **8b** as pale yellow crystals with mp 208–210 °C. IR (ν/cm^{-1}): 1717, 1688 (C=O). ^{1}H NMR (CDCl$_3$) δ: 0.87 (s, 3H, 4'-CH$_3^a$), 1.20 (s, 3H, 4'-CH$_3^b$), 2.53 (d, 2H, 3'-CH$_2^a$, 5'-CH$_2^a$, ^2J 14.2 Hz), 2.68 (br. s, 6H, 10-NMe$_2$), 2.75 (s, 3H, 1-NMe), 2.99 (m, 2H, 3'-CH$_2^b$, 5'-CH$_2^b$), 3.39 (br. s, 2H, 4-CH$_2$), 3.68 (br. s, 2H, 2-CH$_2$), 6.88 (dd, 1H, H-9, ^3J 7.3 Hz, ^4J 1.3 Hz), 7.21 (m, 2H, H-5,8), 7.33 (m, 2H, H-6,7).

8d: was obtained as orange-red oil similar to **8c** by keeping a solution of **6d** (0.07 g, 0.21 mmol) in DMSO (3 ml) at room temperature for 72 h. Yield 0.07 g (100%). IR (ν/cm^{-1}): 2241 (C≡N), 1740 (C=O). ^{1}H NMR (CDCl$_3$) δ: 1.38 (t, 3H, CH$_3$, ^3J 7.3 Hz), 2.83 (br. s, 6H, 10-NMe$_2$), 3.06 (br. s, 3H, 1-NMe), 3.41 (br. d, 1H, 4-CH$_2^c$, ^2J 16.4 Hz), 3.64 (d, 1H, 4-CH$_2^d$, ^2J 16.7 Hz), 3.68 (d, 1H, 2-CH$_2^a$, ^2J 13.0 Hz), 3.94 (br. d, 1H, 2-CH$_2^b$, ^2J 13.3 Hz), 4.34 (q, 2H, OCH$_2$, ^3J 7.3 Hz), 6.94 (dd, 1H, H-9, ^3J 6.6 Hz, ^4J 2.2 Hz), 7.07 (d, 1H, H-5, ^3J 8.2 Hz), 7.23–7.37 (m, 3H, H-6,7,8).

8e: A mixture of **5** (0.07 g, 0.29 mmol) and ethyl cyanoacetate (0.036 g, 0.32 mmol) in MeOH (3 ml) was kept at room temperature for 72 h. After evaporation of the solvent, the residue was treated with *n*-hexane (5 ml) to give **8e** (0.093 g, 99%) as yellow-orange crystals with mp 120–122 °C (from *n*-hexane). IR (ν/cm^{-1}): 2239 (C≡N), 1728 (C=O). ^{1}H NMR (CDCl$_3$) δ: 2.51 (br. s, 3H, 10-NMe$_2^{a}$), 2.81 (br. s, 3H, 10-NMe$_2^{b}$), 3.01 (br. s, 3H, 1-NMe), 3.40 (br. d, 1H, 4-CH$_2^{c}$, ^2J 16.9 Hz), 3.62 (d, 1H, 4-CH$_2^{d}$, ^2J 16.3 Hz), 3.67 (d, 1H, 2-CH$_2^{a}$, ^2J 13.1 Hz), 3.90 (m, 4H, 2-CH$_2^{b}$, OCH$_3$), 6.92 (dd, 1H, H-9, ^3J 6.7 Hz, ^4J 2.3 Hz), 7.13 (d, 1H, H-5, ^3J 8.2 Hz), 7.27–7.35 (m, 3H, H-6,7,8).

10c: A mixture of **9** (0.07 g, 0.26 mmol), ethyl cyanoacetate (0.033 g, 0.29 mmol) and piperidine (0,022 g, 0.26 mmol) in PhMe (6 ml) was kept for 24 h at room temperature and then for 24 h at –20 °C. The separated orange-red crystals of **10c** (0.110 g, 92%) were filtered off, washed with *n*-hexane (3 ml) and dried in air. Mp 129–130 °C. IR (ν/cm^{-1}): 2340, 2362, 2223 (C≡N), 1723(C=O). ^{1}H NMR (CDCl$_3$) δ: 1.39 (t, 6H, CH$_3$, ^3J 7.2 Hz), 3.14 (s, 12H, NMe$_2$), 4.38 (q, 4H, OCH$_2$, ^3J 7.2 Hz), 7.39 (d, 2H, H-3,6, ^3J 8.6 Hz), 7.95 (d, 2H, H-4,5, ^3J 8.6 Hz), 8.39 (s, 2H, –CH=).

11b: was obtained from dialdehyde **9** (0.07 g, 0.26 mmol) and dimedone (0.035 g, 0.26 mmol) similarly to **8b**. Yield 0.129 g (98%). Shine beige crystals, mp 210–212 °C (from MeOH). IR (ν/cm^{-1}): 1682, 1698 (C=O). ^{1}H NMR (CDCl$_3$) δ: 0.87 (s, 6H, 4'-CH$_3^{a}$, 4"-CH$_3^{a}$), 1.17 (s, 6H, 4'-CH$_3^{b}$, 4"-CH$_3^{b}$), 2.62 (s, 6H, NMe), 2.52 (d, 4H, 3'-CH$_2^{a}$, 3"-CH$_2^{a}$, 5'-CH$_2^{a}$, 5"-CH$_2^{a}$, ^2J 13.9 Hz), 2.7–3.2 (m, 6H, 3'-CH$_2^{b}$, 3"-CH$_2^{b}$, 5'-CH$_2^{b}$, 5"-CH$_2^{b}$, 4-CH$_2^{c}$, 9-CH$_2^{c}$), 3.5–3.7 (m, 6H, 2-CH$_2$, 4-CH$_2^{d}$, 9-CH$_2^{d}$, 11-CH$_2$), 7.11 (d, 2H, H-5,8, ^3J 8.2 Hz), 7.28 (d, 2H, H-6,7, ^3J 8.2 Hz).

11c: A solution of **10c** (0.07 g, 0.15 mmol) in DMSO (3 ml) was kept at room temperature for 72 h, providing after evaporation of the solvent pure **11c** (0.07 g, 100%). Orange crystals with mp 157–160 °C (from EtOH). IR (ν/cm^{-1}): 2239 (C≡N), 1736 (C=O). ^{1}H NMR (CDCl$_3$) δ: 1.41 (t, 6H, CH$_3$, ^3J 7.0 Hz), 2.7–3.8 (m, 6H, NMe), 3.45 (d, 2H, 4-CH$_2^{c}$, 9-CH$_2^{c}$, ^2J 16.7 Hz), 3.65 (m, 4H, 4-CH$_2^{d}$, 9-CH$_2^{d}$, 2-CH$_2^{a}$, 11-CH$_2^{a}$), 3.90 (m, 2H, 2-CH$_2^{b}$, 11-CH$_2^{b}$), 4.35 (q, 4H, OCH$_2$, ^3J 7.0 Hz), 7.09 (dd, 2H, H-5, H-8, ^3J 8.2 Hz, ^4J 2.2 Hz), 7.33 (m, 2H, H-6, H-7).