Supporting Information

General: NMR spectra were recorded with an AM 300 Bruker instrument; chemical shifts are δ units downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N). The assignments the chemical shifts are based on experiments, including proton-coupled spectroscopy, selective polarization transfer, 1-D NOE and on calculations.

5-(*tert*-Butyl-*NNO*-azoxy)-6,8-dichlorobenzo-1,2,3,4-tetrazine-1,3-di-N-oxide 7, yellow crystals, m.p. 216—218 °C; ^{1}H NMR (300 MHz, [$^{2}H_6$]acetone) δ 1.51 (s, 9 H, 3 Me), 8.18 (s, 1 H, CH); ^{13}C NMR (76 MHz, [$^{2}H_6$]acetone) δ 25.7 (CH_3), 61.7 ($\underline{C}Me_3$), 126.8 (br, C-8a), 128.7 (^{2}J = 4.5 Hz, C-8), 133.5 (^{1}J = 179 Hz, *C*-7), 135.2 (^{2}J = 4.1 Hz, C-6), 136.2 (br, ^{3}J = 6.3 Hz, C-5), 141.6 (C-4a); ^{14}N NMR (22 MHz, [$^{2}H_6$]acetone) δ –65 (1N, $\Delta\nu_{½}$ = 120 Hz, $\underline{N}$(O)NBu^{t}), –47 (1N, $\Delta\nu_{½}$ = 100 Hz, N→O), –42 (1N, $\Delta\nu_{½}$ = 30 Hz, N→O); EI-MS, *m/z* 261, 263, 265 (9 : 6 : 1) (M–NBu^{t+}).

6-Amino-5-(*tert*-Butyl-*NNO*-azoxy)-8-chlorobenzo-1,2,3,4-tetrazine-1,3-di-N-oxide 8, yellow crystals, m.p. 261—263 °C; ^{1}H NMR (300 MHz, [$^{2}H_6$]acetone) δ 1.48 (s, 9 H, 3 Me), 6.9 (br, 2 H, NH_2), 7.47 (s, 1 H, CH); ^{13}C NMR (76 MHz, [$^{2}H_6$]DMSO) δ 25.6 (CH_3), 60.1 ($\underline{C}Me_3$), 117.8 (br, C-8a), 119.7 (br, C-5), 123.2 (C-7), 126.7 (C-8), 142.1 (C-4a), 146.6 (C-6); ^{14}N NMR (22 MHz, [$^{2}H_6$]acetone) δ –62 (1N, $\Delta\nu_{½}$ = 90 Hz, $\underline{N}$(O)NBu^{t}), –45 (2N, $\Delta\nu_{½}$ = 50 Hz, 2 N→O); EI-MS, *m/z* 313, 315 (3 : 1) (M^{+}).

8-Amino-5-(*tert*-Butyl-*NNO*-azoxy)-6-chlorobenzo-1,2,3,4-tetrazine-1,3-di-N-oxide 9, red crystals, decomp. > 280 °C; ^{1}H NMR (300 MHz, [$^{2}H_6$]acetone) δ 1.47 (s, 9 H, 3 Me), 7.18 (s, 1 H, CH), 8.0 (br, 2 H, NH_2); ^{13}C NMR (76 MHz, [$^{2}H_6$]DMSO) δ 25.2 (CH_3), 59.8 ($\underline{C}Me_3$), 111.4 (C-7), 115.1 (br, C-8a), 125.1 (br, C-5), 135.2 (C-6), 138.8 (C-4a), 144.4 (C-8); ^{14}N NMR (22 MHz, [$^{2}H_6$]acetone) δ –62 (1N, $\Delta\nu_{½}$ = 100 Hz, $\underline{N}$(O)NBu^{t}), –47 (1N, $\Delta\nu_{½}$ = 100 Hz, N→O), –38 (1N, $\Delta\nu_{½}$ = 60 Hz, N→O); EI-MS, *m/z* 313, 315 (3 : 1) (M^{+}).

8-Amino-6-chloro-5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-di-N-oxide 14, red crystals, m.p. 153—155 °C; ^{1}H NMR (300 MHz, [$^{2}H_6$]acetone) δ 8.9 (br, 2 H, NH_2); ^{13}C NMR (76 MHz, [$^{2}H_6$]acetone) δ 118.4 (br, C-8a), 132.0 (C-6), 140.5 (C-8), 141.7 (C-4a); ^{14}N NMR (22 MHz, [$^{2}H_6$]acetone) δ –43 (1N, $\Delta\nu_{½}$ = 55 Hz, N→O), –37 (1N, $\Delta\nu_{½}$ = 40 Hz, N→O), –22 (1N, $\Delta\nu_{½}$ = 90 Hz, NO_2), –20 (1N, $\Delta\nu_{½}$ = 100 Hz, NO_2); EI-MS, *m/z* 303, 305 (3 : 1) (M^{+}).