

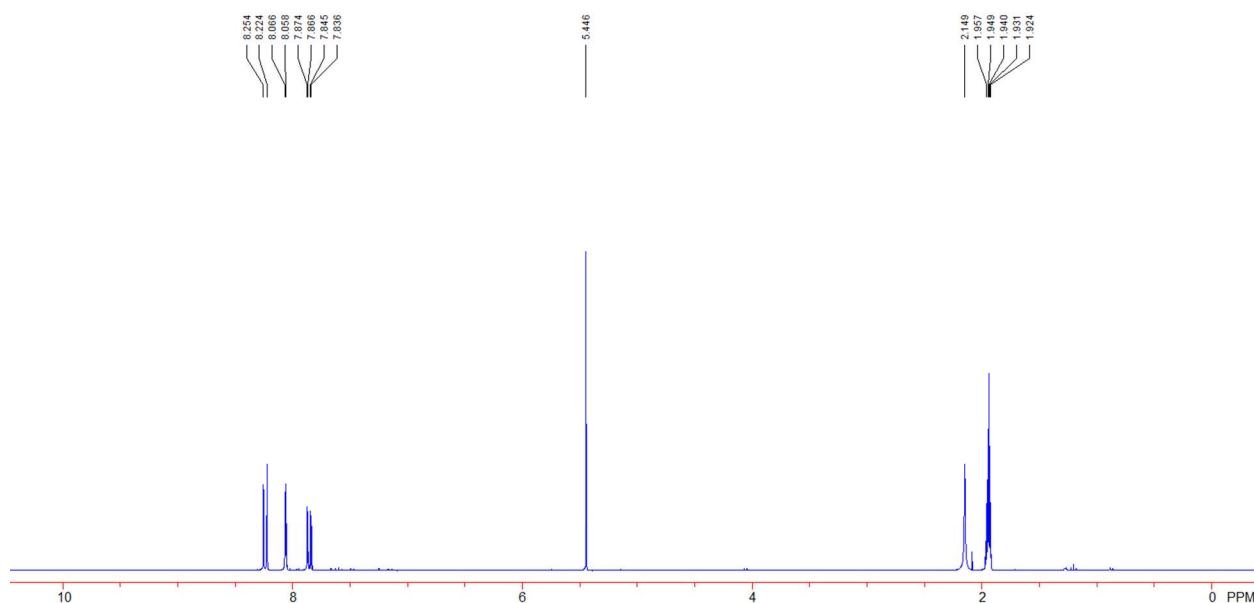
Supporting Information for “Photoactive High Explosives: Substituents Effects on Tetrazine Photochemistry and Photophysics”

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Synthesis of DNP-Tz-Cl (6).

In a small vial, 3,4-dinitrophenol (0.146 g, 0.793 mmol) and NaOH (790 μ l of a 40 mg/ml solution, 0.79 mmol) were combined in water (2 ml). The solvent was allowed to evaporate, and then the remaining yellow solid was suspended in CH₃CN (5 ml). To the suspension was added 3,6-dichlorotetrazine (0.119 g, 0.793 mmol) and the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum, and the remaining dark red residue was purified by silica gel chromatography (CH₂Cl₂), affording compound **6** as an orange-red solid (Yield: 26%). ¹H NMR (300 MHz, CD₃CN): δ 8.24 (d, 1H, J = 9.0 Hz), 8.06 (d, 1H, J = 2.4 Hz), 7.85 (dd, 1H, J = 9.0 Hz, J = 2.4 Hz). ¹³C{¹H} NMR (75 MHz, CD₃CN): 168.2, 166.9, 155.6, 144.9, 141.3, 129.0, 127.5, 119.8.



Synthesis of DNAZ-Tz-Cl (2)

3-Chloro-6-[(3,3-dinitro)-1-azetidiny]-1,2,4,5-tetrazine. 3,6-Dichloro-1,2,4,5-tetrazine (0.151 g, 1.0 mmol) was dissolved in acetonitrile and 3,3-dinitroazetidine (0.294 g, 2.0 mmol) was added.

The mixture was allowed to stir for 1 h at ambient temperature, during which time 3,3-dinitroazetidinium hydrochloride precipitated from solution. The mixture was filtered and the solvent removed a crystalline, orange product (0.265 g, 98%): mp. 177-179 °C (dec.); ¹H NMR (DMSO-*d*₆) δ 5.25 (s, 4H); ¹³C NMR (DMSO-*d*₆) δ 59.7, 108.1, 161.6, 163.2; IR (KBr) 3003, 2953, 1591, 1533, 1458, 1447, 1371, 1338, 1306, 1216, 1137, 1052, 945, 929 cm⁻¹.

Synthesis of DNAZ-Tz-DNAZ (1)

3,6-bis[(3,3-Dinitro)-1-azetidiny]-1,2,4,5-tetrazine. Triethylamine (0.70 g, 6.90 mmol) was added to stirred solution of 3,3-dinitroazetide (1.0 g, 3.37 mmol) in acetonitrile (10 mL), and this addition was followed by slow addition of 3,6-dichloro-1,2,4,5-tetrazine (0.166 g, 1.10 mmol). The reaction mixture was slowly brought to a reflux over 2 h and allowed to reflux another 4 h. After cooling to ambient temperature, the reaction was poured into water and allowed to stand overnight to agglomerate. The red precipitate was collected by filtration, air dried and recrystallized from ethyl acetate/hexanes, affording a red solid (0.60 g, 15%) mp. 230 °C (dec.); ¹H NMR (DMSO-*d*₆) δ 5.13 (s, 8H); ¹³C NMR (DMSO-*d*₆) δ 59.4, 108.2, 162.4; IR (KBr) 3009, 2964, 1586, 1564, 1484, 1445, 1369, 1335, 1302, 1057, 945, 839 cm⁻¹.

The synthesis of DNAZ-Tz-azo-Tz-DNAZ (5) is currently being prepared for separate publication by D. E. Chavez and co-workers.