Electronic Supplementary Information

Energetic Aminated-azole Assembly from Intramolecular and Intermolecular N-H…O and N-H…N Hydrogen Bonds

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Experimental Section

Caution: All the nitrogen-rich compounds are energetic materials and may explode under certain conditions and amines are potentially toxic. Appropriate safety precautions should be taken when preparing and handling. Eye protection and leather gloves must be worn at all times. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

General Methods

Reagents were purchased from AKSci, Aldrich and Acros Organics and were used as received. ^{1}H, and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for ^{15}N spectra using DMSO-d_6 as solvent and locking solvent unless otherwise stated. Chemical shifts in ^{1}H, ^{13}C and ^{15}N NMR spectra are reported relative to Me_4Si and $MeNO_2$, respectively. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q20) at a scan rate of 5 °C/min. IR spectra were recorded using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer.

Ammonium 5-amino-2,4-dinitroimidazolate, 1: Compound **1** was prepared using a procedure similar to that for 4-nitro-5-aminoimidazole[1] by heating ammonium 2,4,5-trinitroimidazolate (3.3 g, 15 mmol) with concentrated aqueous ammonia (20 mL) in a sealed tube at 50-55 °C. A red solid precipitated slowly from the clear yellow solution. The reaction mixture was allowed to stir for 4 days at 50 °C. The reaction was then cooled to room temperature and the red solid was collected by filtration. It was washed with ice-water (3×5 mL) and air dried to give 1.48 g of **1** (52%). T_{dec} (onset): 222.4 °C; IR (cm^{-1}) υ = 3459, 3343, 3234, 3143, 1682, 1619, 1548, 1493, 1426, 1301, 1221, 1177, 1065, 1005, 863, 812, 754, 638, 480; ^{1}H NMR: δ 7.14 (4H, s, NH_4^+); δ 6.41 (2H, s, NH_2) ppm; ^{13}C NMR: δ 131.5 (C5), 151.0 (C4), 151.5 (C2) ppm. Elemental analyses ($C_3H_6N_6O_4$, 190.12): Calcd, C: 18.95; H: 3.18; N: 44.20; Found, C: 18.86; H: 3.13; N: 43.55.

5-Amino-2,4-dinitroimidazole monohydrate, 2: Compound **1** (0.19 g, 1 mmol) was suspended in water (5 mL), then acidified with 1M HCl solution (5 mL). The color of the solid changed from red to yellow, the precipitate was collected by filtration, washed with ice-water (3 x 3 mL), and air dried to give 0.17 g of **2** (89.5%). T_{dec} (onset): 108.9 °C; IR (cm^{-1}) υ = 3557, 3461, 3354, 1662, 1522, 1446, 1414, 1327, 1279, 1244, 1188, 993, 906, 867, 818, 756, 740, 696, 628, 536, 495, 440; ^{1}H NMR (CD_3CN): δ 6.61 (2H, s, NH_2) ppm; ^{13}C NMR (CD_3CN): δ 128.7(C5), 137.6(C4), 143.7(C2) ppm. Elemental analyses ($C_3H_3N_5O_4 \cdot H_2O$, 191.10): Calcd, C: 18.85; H: 2.64; N: 36.65; Found, C: 18.83; H: 2.61; N: 36.55.

1,5-Diamino-2,4-dinitroimidazole, 3: To a solution of **2** (0.38 g, 2 mmol) in acetonitrile (10 mL) was added DBU (0.30 g, 2 mmol), and the reaction mixture was stirred for 30 min at room temperature. Then freshly prepared O-*p*-toluenesulfonylhydroxylamine[2] (THA) (0.47g, 2.5 mmol) in dichloromethane (10 mL) was added in one portion, and the reaction mixture was stirred for 30 min at room temperature. The solvent was removed and the residue was

suspended in cold water (10 mL). The precipitate formed was collected by filtration to obtain 0.26 g of **3**, yield: 69.1%. T_{dec} (onset): 202.5 °C; IR (cm^{-1}) υ = 3395, 3331, 3275, 3229, 1650, 1599, 1558, 1514, 1473, 1335, 1302, 1281, 1223, 1057, 997, 890, 817, 773, 756, 613, 532; ^{1}H NMR: δ 7.85 (2H, s, N-NH_2); 6.16 (2H, s, C-NH_2) ppm; ^{13}C NMR: δ 122.9 (C5); 136.8 (C4); 144.4 (C2) ppm; ^{15}N NMR (DMSO-d_6): -20.19 (C4-$\underline{NO_2}$), -30.20 (C2-$\underline{NO_2}$), -137.18 (N3), 221.78 (N1), 309.68 (t, C-$\underline{NH_2}$), 311.13 (t, N-$\underline{NH_2}$) ppm. Elemental analyses ($C_3H_4N_6O_4$, 188.10): Calcd, C: 19.16; H: 2.14; N: 44.68; Found, C: 19.52; H: 2.10; N: 43.32.

Amination of 4-amino-5-nitro-1,2,3-2*H*-triazole: A mixture of 4-amino-5-nitro-1,2,3-2*H*-triazole[3] (1.29 g, 10 mmol) and 1,8-diazabicycloundec-7-ene (DBU) (1.52 g, 10 mmol) in acetonitrile (20 mL) was stirred for 30 min at room temperature. This was followed by the addition of freshly prepared O-*p*-toluenesulfonylhydroxylamine (1.1 eq) in dichloromethane (20 mL) in one portion. After stirring for 30 min, the solvent was removed under vacuum and the residue was extracted with ethyl acetate (3x10 mL). Compounds **5** and **6** can be isolated by column chromatography (ethyl acetate/hexane = 5/5). Compound **6** was the major product (0.52 g, yield: 36.1%), **5** (0.31 g, yield: 21.5%), and trace amounts of **4,** mixed with **5**, was detected via proton NMR.

1,4-Diamino-5-nitro-1,2,3-triazole, 4: yellow solid, trace amount. ^{1}H NMR (CD_3CN): δ 5.78 (2H, s, NH_2), 6.39 (2H, s, NH_2) ppm.

2,4-Diamino-5-nitro-1,2,3-triazole, 5: yellow solid, yield: 21.5%. T_{dec} (onset): 212.1 °C; IR (cm^{-1}) υ = 3443, 3339, 3255, 1644, 1578, 1518, 1457, 1424, 1396, 1350, 1209, 1175, 1068, 976, 913, 837, 722, 644, 434; ^{1}H NMR (CD_3CN): δ 5.64 (2H, s, NH_2), 6.55 (2H, s, NH_2) ppm; ^{13}C NMR: δ 137.6 (C5), 143.6 (C4) ppm; Elemental analyses ($C_2H_4N_6O_2$, 144.09): Calcd, C: 16.67; H: 2.80; N: 58.32; Found, C: 16.79; H: 2.79; N: 57.97.

3,4-Diamino-5-nitro-1,2,3-triazole, 6: white solid, yield: 36.1%. m.p.: 189.6 °C, T_{dec} (onset): 204.9 °C; IR (cm^{-1}) υ = 3416, 3356, 3300, 1677, 1614, 1562, 1461, 1402, 1329, 1304, 1255, 986, 895, 835, 761, 708, 572, 522; ^{1}H NMR (CD_3CN): δ 5.66 (2H, s, NH_2), 6.30 (2H, s, NH_2) ppm; ^{13}C NMR: δ 136.6 (C5), 142.1 (C4) ppm; ^{15}N NMR (CD3CN/CH_3OH): -21.66 (C5-$\underline{NO_2}$), -33.62 (N2), -44.78 (N1), -152.19 (N3), -310.50 (C4-$\underline{NH_2}$), -324.50 (N-$\underline{NH_2}$) ppm. Elemental analyses ($C_2H_4N_6O_2$, 144.09): Calcd, C: 16.67; H: 2.80; N: 58.32; Found, C: 16.94; H: 2.78; N: 57.72.

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Table S1. Crystal data and structure refinement for **3** **6**.

	3	**4**	**5**	**6**
Empirical formula	$C_3H_4N_6O_4$	$C_2H_4N_6O_2$	$C_2H_4N_6O_2$	$C_2H_4N_6O_2$
Formula weight	188.12	144.11	144.11	144.11
Temperature/K	150(2) K	150(2) K	296(2) K	150(2) K
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pna2₁*	*C2/c*	*P2₁*	*P2₁/n*
a/Å	12.7338(4)	12.8179(10)	3.5852(3)	8.0055(7)
b/Å	9.9770(3)	4.8463(3)	16.3937(12)	6.4742(6)
c/Å	5.1360(2)	18.2472(12)	9.4278(7)	10.7844(10)
α/°	90	90	90	90
β/°	90	100.494(3)°	98.448(3)°	96.2240(10)°
γ/°	90	90	90	90
Volume/Å^3	652.50(4)	1114.55(13)	548.10(7)	555.65(9)
Z	4	8	4	4
ρ_{calc} g/cm^3	1.915 (-123 ºC) , 1.873 (20 ºC)	1.718 (-123 ºC), 1.676 (20 ºC)	1.746 (-123 ºC)	1.723 (-123 ºC)
μ/mm^{-1}	1.549	0.149 mm-1	0.152 mm-1	0.150 mm-1
F(000)	384.0	592	296	296
Crystal size/mm^3	0.16 x 0.11 x 0.02	0.267 x 0.226 x 0.049	0.162 x 0.025 x 0.005	0.427 x 0.397 x 0.089
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.63 to 68.18°.	3.233 to 27.507°.	2.184 to 26.474°	3.018 to 27.543°.
Index ranges	-15<=h<=14, -8<=k<=11, -6<=l<=5	-16<=h<=16, -5<=k<=6, -23<=l<=23	-4<=h<=4, -20<=k<=20, -11<=l<=11	-10<=h<=10, -7<=k<=8, -13<=l<=14
Reflections collected	3278	5450	5324	5123
Independent reflections	1058 [R_{int} = 0.0388]	1285 [$R_{(int)}$ = 0.0199]	2257 [$R_{(int)}$ = 0.0483]	1290 [$R_{(int)}$ = 0.0143]
Data/restraints/parameters	1058 / 3 / 124	1285 / 0 / 103	2257 / 9 / 206	1290 / 0 / 103
Goodness-of-fit on F^2	1.066	1.014	1.045	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0882	R_1 = 0.0279, wR_2 = 0.0699	R_1 = 0.0480, wR_2 = 0.0897	R_1 = 0.0312, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0882	R_1 = 0.0334, wR_2 = 0.0738	R_1 = 0.0918, wR_2 = 0.1114	R_1 = 0.0326, wR_2 = 0.0869
Largest diff. peak/hole / e Å^{-3}	00.225 and -0.226 e.Å^{-3}	0.315 and -0.201 e.Å^{-3}	0.194 and -0.208 e.Å^{-3}	0.259 and -0.341 e.Å^{-3}
CCDC number	1463785	1463784	1463786	1463787

Table S2. Bond lengths [Å] and angles [°] for **3**.

N(1)-C(5)	1.362(3)
N(1)-C(2)	1.386(3)
N(1)-N(6)	1.409(2)
C(2)-N(3)	1.310(3)
C(2)-N(7)	1.420(3)
N(3)-C(4)	1.356(3)
C(4)-N(10)	1.405(3)
C(4)-C(5)	1.406(2)
C(5)-N(13)	1.339(3)
N(6)-H(6A)	0.8500(11)
N(6)-H(6B)	0.8501(11)
N(7)-O(9)	1.226(2)
N(7)-O(8)	1.233(2)
N(10)-O(12)	1.238(2)
N(10)-O(11)	1.240(2)
N(13)-H(13A)	0.8800
N(13)-H(13B)	0.8800
C(5)-N(1)-C(2)	106.73(16)
C(5)-N(1)-N(6)	121.15(16)
C(2)-N(1)-N(6)	132.12(18)
N(3)-C(2)-N(1)	113.10(19)
N(3)-C(2)-N(7)	123.14(17)
N(1)-C(2)-N(7)	123.76(17)
C(2)-N(3)-C(4)	103.94(15)
N(3)-C(4)-N(10)	121.84(16)
N(3)-C(4)-C(5)	112.26(17)
N(10)-C(4)-C(5)	125.86(18)
N(13)-C(5)-N(1)	122.96(17)
N(13)-C(5)-C(4)	133.02(19)
N(1)-C(5)-C(4)	103.96(16)
N(1)-N(6)-H(6A)	105.5(17)
N(1)-N(6)-H(6B)	102.7(18)
H(6A)-N(6)-H(6B)	118(3)
O(9)-N(7)-O(8)	124.41(18)
O(9)-N(7)-C(2)	118.08(16)
O(8)-N(7)-C(2)	117.51(16)
O(12)-N(10)-O(11)	123.79(17)
O(12)-N(10)-C(4)	117.11(16)
O(11)-N(10)-C(4)	119.09(17)
C(5)-N(13)-H(13A)	120.0
C(5)-N(13)-H(13B)	120.0
H(13A)-N(13)-H(13B)	120.0

Table S3. Bond lengths [Å] and angles [°] for **4**.

O(1)-N(3)	1.2322(12)
O(2)-N(3)	1.2440(12)
N(3)-C(4)	1.3966(14)
C(4)-N(9)	1.3724(14)
C(4)-C(5)	1.3907(15)
C(5)-N(6)	1.3433(15)
C(5)-N(7)	1.3653(14)
N(6)-H(6A)	0.874(15)
N(6)-H(6B)	0.876(16)
N(7)-N(8)	1.3277(13)
N(8)-N(9)	1.3188(13)
N(9)-N(10)	1.3977(13)
N(10)-H(10A)	0.878(16)
N(10)-H(10B)	0.911(15)
O(1)-N(3)-O(2)	124.08(9)
O(1)-N(3)-C(4)	119.96(9)
O(2)-N(3)-C(4)	115.97(9)
N(9)-C(4)-C(5)	105.30(9)
N(9)-C(4)-N(3)	124.80(9)
C(5)-C(4)-N(3)	129.90(10)
N(6)-C(5)-N(7)	122.38(10)
N(6)-C(5)-C(4)	130.90(10)
N(7)-C(5)-C(4)	106.71(9)
C(5)-N(6)-H(6A)	118.1(9)
C(5)-N(6)-H(6B)	121.0(9)
H(6A)-N(6)-H(6B)	116.0(13)
N(8)-N(7)-C(5)	109.42(9)
N(9)-N(8)-N(7)	108.31(9)
N(8)-N(9)-C(4)	110.25(9)
N(8)-N(9)-N(10)	118.08(9)
C(4)-N(9)-N(10)	131.44(9)
N(9)-N(10)-H(10A)	108.0(9)
N(9)-N(10)-H(10B)	106.8(9)
H(10A)-N(10)-H(10B)	108.8(13)

Table S4. Bond lengths [Å] and angles [°] for **5**.

N(1A)-N(5A)	1.338(6)	N(1A)-C(2A)	1.357(7)
C(2A)-N(6A)	1.327(7)	C(2A)-C(3A)	1.388(8)
C(3A)-N(4A)	1.363(7)	C(3A)-N(7A)	1.398(7)
N(4A)-N(5A)	1.288(6)	N(5A)-N(10A)	1.380(6)
N(6A)-H(6A)	0.871(15)	N(6A)-H(6B)	0.865(15)
N(7A)-O(8A)	1.233(6)	N(7A)-O(9A)	1.252(6)
N(10A)-H(10A)	0.870(15)	N(10A)-H(10B)	0.877(15)
N(1B)-N(5B)	1.336(6)	N(1B)-C(2B)	1.354(7)
C(2B)-N(6B)	1.339(7)	C(2B)-C(3B)	1.406(8)
C(3B)-N(4B)	1.347(7)	C(3B)-N(7B)	1.395(7)
N(4B)-N(5B)	1.300(6)	N(5B)-N(10B)	1.393(6)
N(6B)-H(6C)	0.862(15)	N(6B)-H(6D)	0.877(15)
N(7B)-O(8B)	1.232(6)	N(7B)-O(9B)	1.236(6)
N(10B)-H(10C)	0.872(15)	N(10B)-H(10D)	0.865(15)
N(5A)-N(1A)-C(2A)	103.3(4)	N(6A)-C(2A)-N(1A)	122.5(5)
N(6A)-C(2A)-C(3A)	131.3(6)	N(1A)-C(2A)-C(3A)	106.3(5)
N(4A)-C(3A)-C(2A)	110.8(5)	N(4A)-C(3A)-N(7A)	120.6(5)
C(2A)-C(3A)-N(7A)	128.6(5)	N(5A)-N(4A)-C(3A)	101.5(4)
N(4A)-N(5A)-N(1A)	118.1(4)	N(4A)-N(5A)-N(10A)	122.3(4)
N(1A)-N(5A)-N(10A)	119.1(4)	C(2A)-N(6A)-H(6A)	114(4)
C(2A)-N(6A)-H(6B)	109(4)	H(6A)-N(6A)-H(6B)	136(6)
O(8A)-N(7A)-O(9A)	124.0(5)	O(8A)-N(7A)-C(3A)	117.3(5)
O(9A)-N(7A)-C(3A)	118.7(5)	N(5A)-N(10A)-H(10A)	109(4)
N(5A)-N(10A)-H(10B)	120(4)	H(10A)-N(10A)-H(10B)	98(6)
N(5B)-N(1B)-C(2B)	102.3(4)	N(6B)-C(2B)-N(1B)	121.5(5)
N(6B)-C(2B)-C(3B)	131.3(5)	N(1B)-C(2B)-C(3B)	107.2(4)
N(4B)-C(3B)-N(7B)	120.7(5)	N(4B)-C(3B)-C(2B)	110.0(5)
N(7B)-C(3B)-C(2B)	129.2(5)	N(5B)-N(4B)-C(3B)	101.8(4)
N(4B)-N(5B)-N(1B)	118.7(4)	N(4B)-N(5B)-N(10B)	121.8(4)
N(1B)-N(5B)-N(10B)	118.9(4)	C(2B)-N(6B)-H(6C)	120(4)
C(2B)-N(6B)-H(6D)	114(4)	H(6C)-N(6B)-H(6D)	123(6)
O(8B)-N(7B)-O(9B)	124.0(5)	O(8B)-N(7B)-C(3B)	119.5(5)
O(9B)-N(7B)-C(3B)	116.5(5)	N(5B)-N(10B)-H(10C)	98(4)
N(5B)-N(10B)-H(10D)	108(5)	H(10C)-N(10B)-H(10D)	123(6)

Table S5. Bond lengths [Å] and angles [°] for **6**.

O(1)-N(3)	1.2401(12)
O(2)-N(3)	1.2422(12)
N(3)-C(4)	1.4005(13)
C(4)-N(10)	1.3620(13)
C(4)-C(5)	1.3986(13)
C(5)-N(6)	1.3291(13)
C(5)-N(7)	1.3483(12)
N(6)-H(6A)	0.850(16)
N(6)-H(6B)	0.851(16)
N(7)-N(9)	1.3824(12)
N(7)-N(8)	1.3882(12)
N(8)-H(8A)	0.889(16)
N(8)-H(8B)	0.876(16)
N(9)-N(10)	1.2919(13)
O(1)-N(3)-O(2)	123.30(9)
O(1)-N(3)-C(4)	119.74(9)
O(2)-N(3)-C(4)	116.94(9)
N(10)-C(4)-C(5)	110.55(9)
N(10)-C(4)-N(3)	122.60(9)
C(5)-C(4)-N(3)	126.70(9)
N(6)-C(5)-N(7)	123.58(9)
N(6)-C(5)-C(4)	134.43(9)
N(7)-C(5)-C(4)	101.99(8)
C(5)-N(6)-H(6A)	118.3(10)
C(5)-N(6)-H(6B)	120.4(10)
H(6A)-N(6)-H(6B)	121.3(14)
C(5)-N(7)-N(9)	111.69(8)
C(5)-N(7)-N(8)	123.26(9)
N(9)-N(7)-N(8)	124.99(8)
N(7)-N(8)-H(8A)	105.8(9)
N(7)-N(8)-H(8B)	109.4(10)
H(8A)-N(8)-H(8B)	112.6(13)
N(10)-N(9)-N(7)	107.48(8)
N(9)-N(10)-C(4)	108.29(8)

Table S6. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(12)#1	0.8500(11)	2.52(2)	3.087(2)	125(2)
N(13)-H(13A)...N(6)	0.88	2.52	2.821(2)	100.8
N(13)-H(13B)...O(12)	0.88	2.36	2.873(2)	117.1

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1

Table S7. Hydrogen bonds for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...N(7)#1	0.874(15)	2.154(16)	3.0113(14)	166.7(13)
N(6)-H(6B)...O(2)	0.876(16)	2.439(14)	2.9193(13)	115.1(11)
N(6)-H(6B)...N(10)#2	0.876(16)	2.156(16)	3.0173(14)	167.5(13)
N(10)-H(10A)...N(6)#3	0.878(16)	2.420(16)	3.2633(15)	161.2(13)
N(10)-H(10B)...O(2)#4	0.911(15)	2.186(15)	3.0952(13)	174.9(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x+1/2,y+1/2,z #3 x-1/2,y+1/2,z

#4 -x+1/2,y-1/2,-z+1/2

Table S8. Hydrogen bonds for **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6A)-H(6A)...O(8A)	0.871(15)	2.32(5)	2.902(7)	125(5)
N(6A)-H(6A)...O(8B)#1	0.871(15)	2.27(4)	3.017(7)	143(6)
N(6A)-H(6B)...N(1B)#2	0.865(15)	2.248(18)	3.110(7)	174(6)
N(10A)-H(10A)...N(4B)#3	0.870(15)	2.43(4)	3.170(7)	143(6)
N(10A)-H(10A)...O(8B)#3	0.870(15)	2.47(5)	3.121(6)	132(5)
N(10A)-H(10B)...O(8A)#4	0.877(15)	2.08(3)	2.923(6)	160(6)
N(6B)-H(6C)...O(9A)#5	0.862(15)	2.25(3)	3.052(7)	154(6)
N(6B)-H(6C)...O(9B)	0.862(15)	2.43(5)	2.925(7)	117(5)
N(6B)-H(6D)...N(1A)#6	0.877(15)	2.202(18)	3.075(7)	174(6)
N(10B)-H(10C)...O(9B)#7	0.872(15)	2.37(5)	3.004(6)	130(5)
N(10B)-H(10D)...N(4A)#8	0.865(15)	2.41(4)	3.173(6)	148(6)
N(10B)-H(10D)...O(9A)#8	0.865(15)	2.49(5)	3.134(6)	132(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z #2 x,y,z-1 #3 x-1,y,z #4 -x,y-1/2,-z

#5 -x,y-1/2,-z+1 #6 x,y,z+1 #7 -x+1,y+1/2,-z+1

#8 x+1,y,z

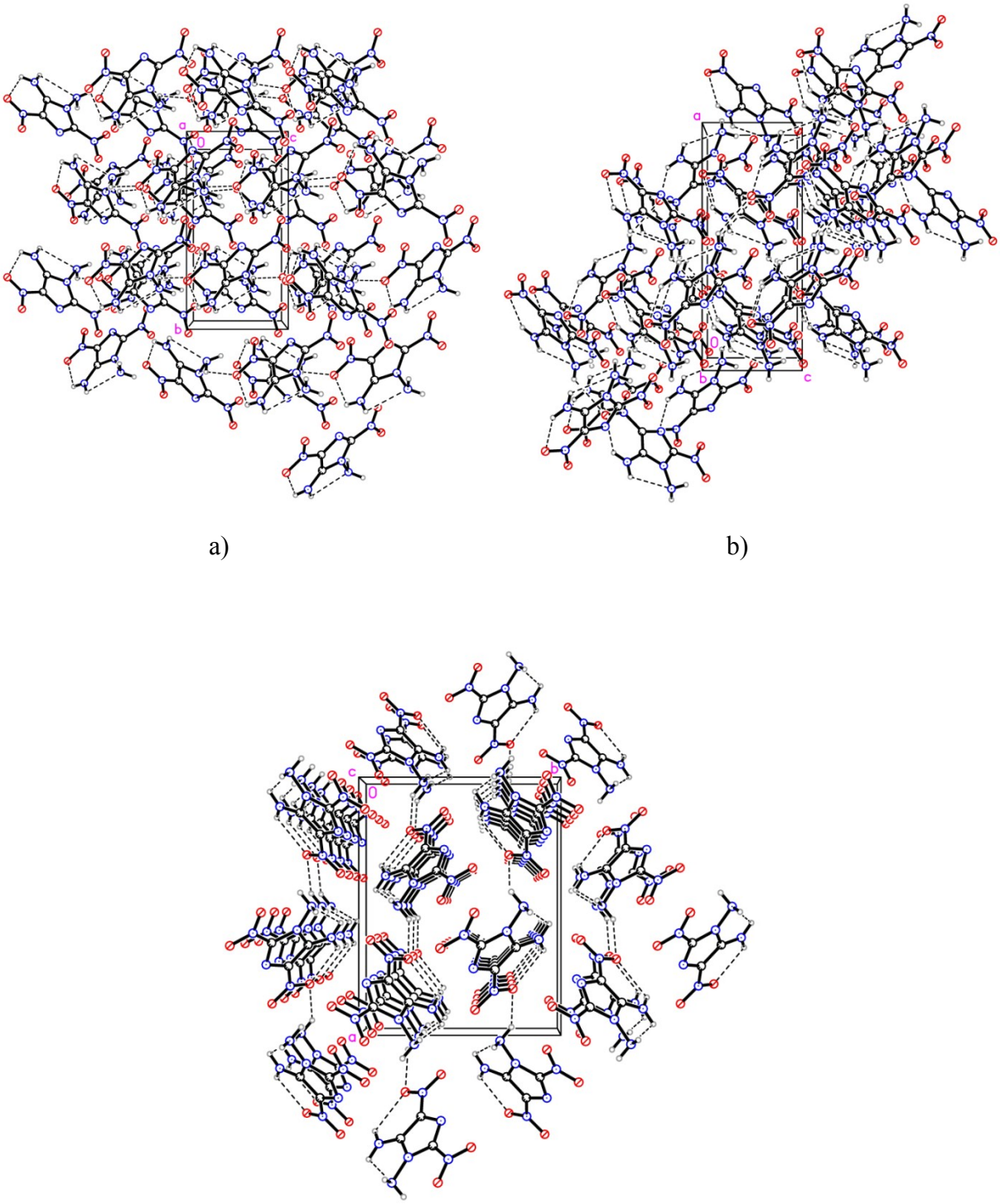
Table S9. Hydrogen bonds for **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(1)#1	0.850(16)	2.170(16)	2.9620(12)	154.9(13)
N(6)-H(6B)...O(2)	0.851(16)	2.442(16)	2.9189(13)	116.1(12)
N(6)-H(6A)...N(8)	0.850(16)	2.542(14)	2.8458(13)	102.2(11)
N(6)-H(6B)...N(9)#2	0.851(16)	2.261(16)	3.0664(13)	158.0(14)
N(8)-H(8A)...N(10)#3	0.889(16)	2.266(15)	3.0188(14)	142.4(13)
N(8)-H(8B)...O(2)#4	0.876(16)	2.337(15)	3.0082(12)	133.5(13)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z-1/2 #2 x-1/2,-y+3/2,z-1/2

#3 -x+3/2,y+1/2,-z+3/2 #4 x+1,y,z



a) b)

c)

Figure S1 Packing diagram of **3** viewed along *a*, *b* and *c*-axes at the 50% probability level.

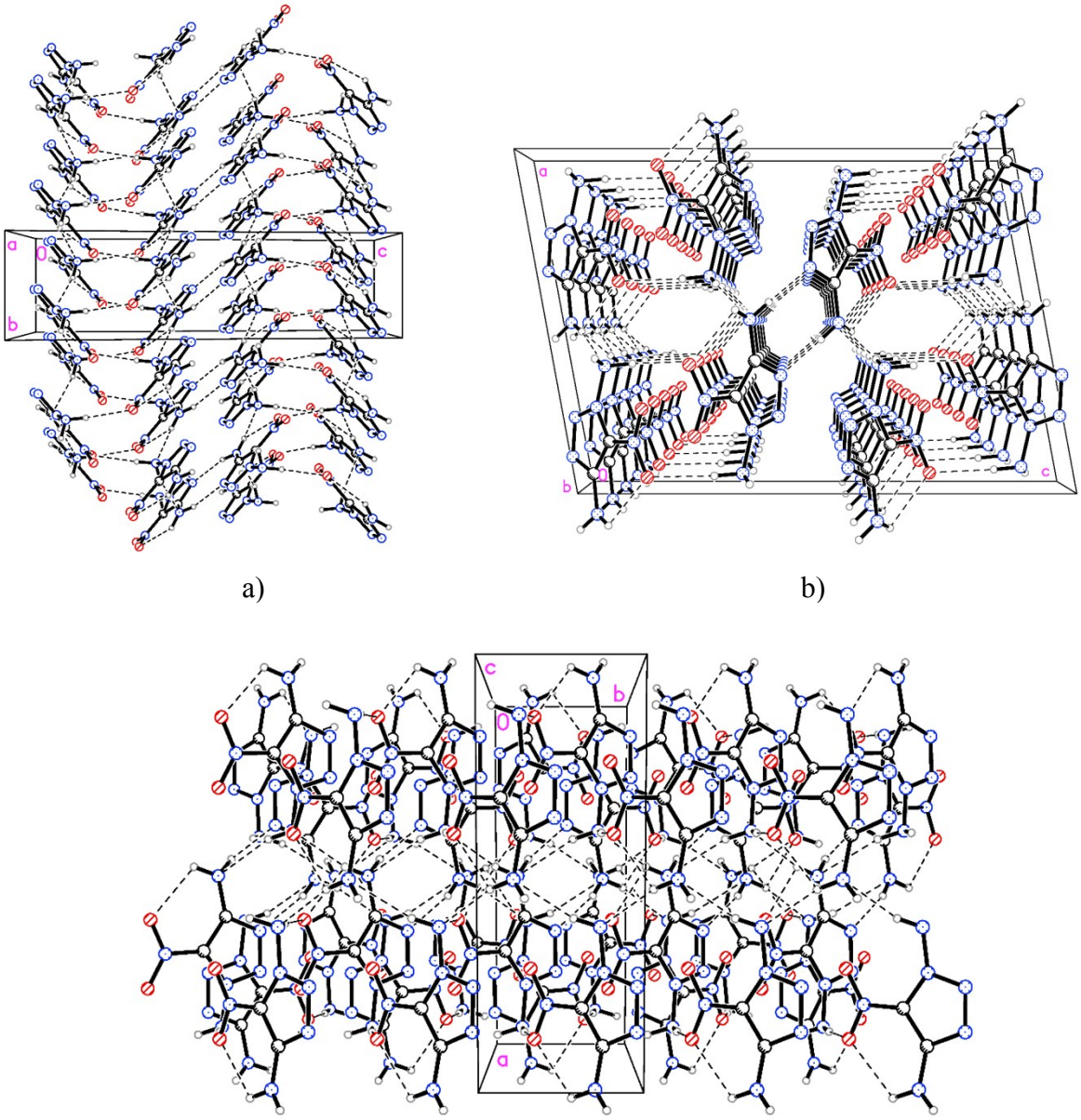
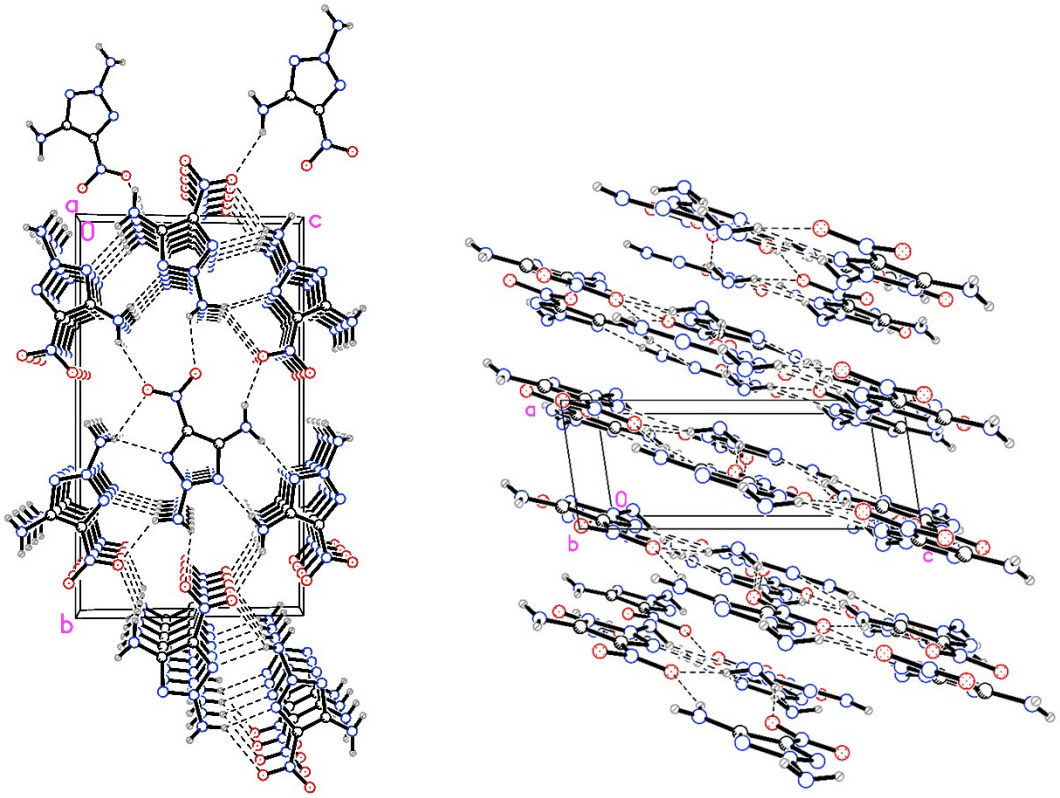


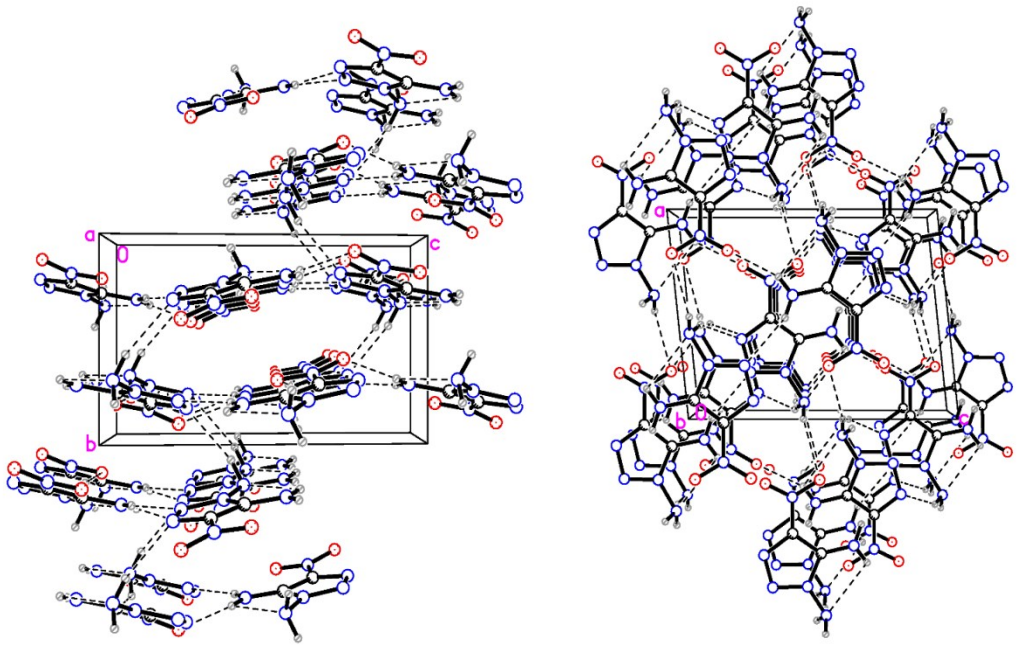
Figure S2 Packing diagram of compound **4** viewing along *a*, *b* and *c*-axes at the 50% probability level.



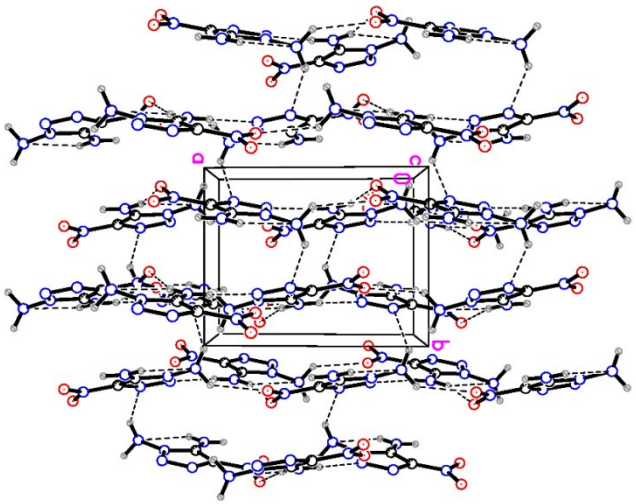
a) b)

c)

Figure S3 Packing diagram of compound **5** viewing along *a*, *b* and *c*-axes at the 50% probability level.

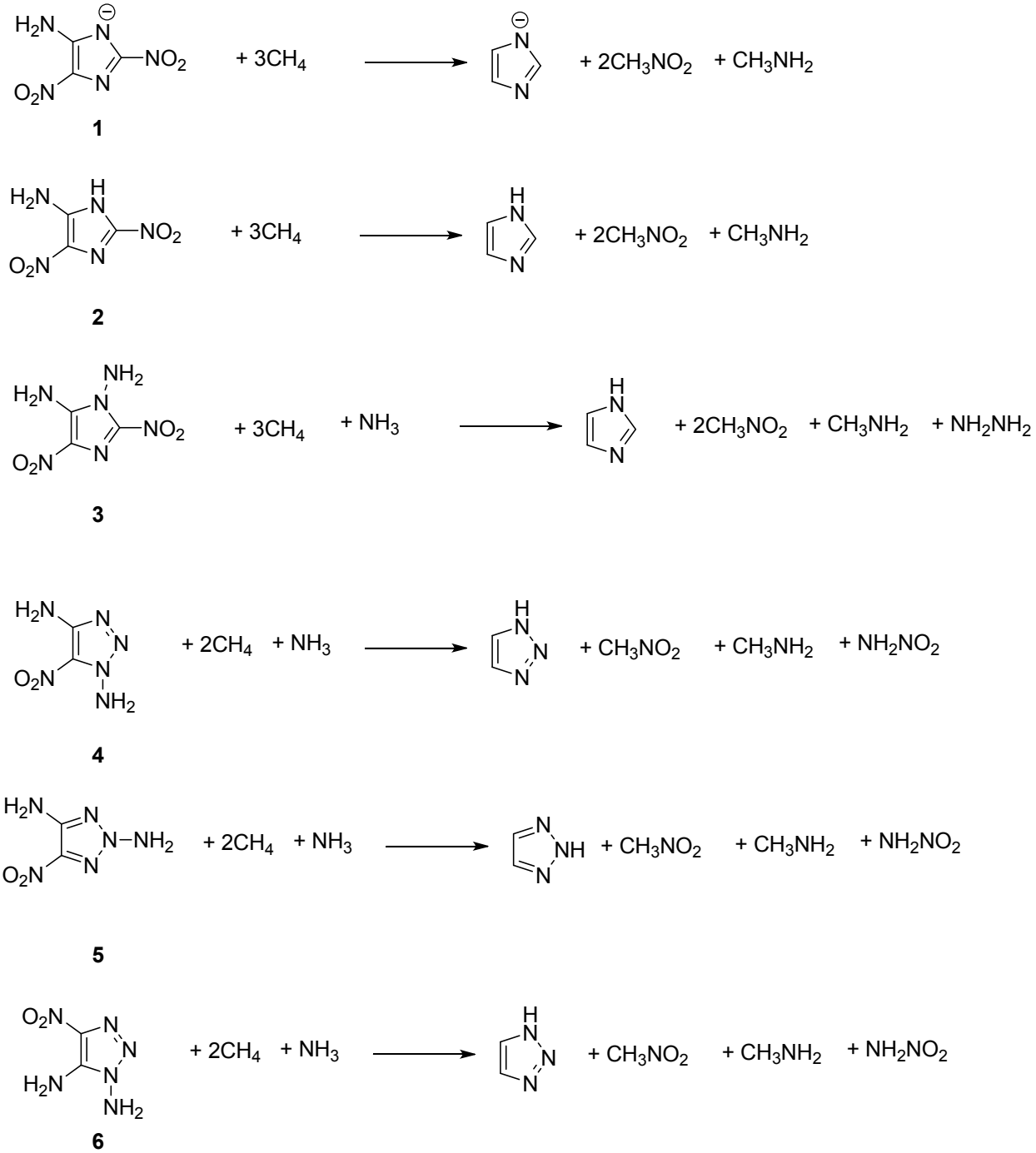


a) b)



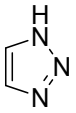
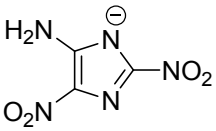
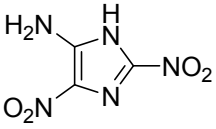
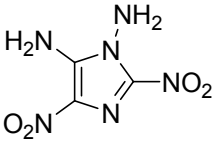
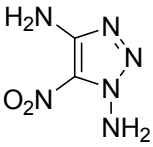
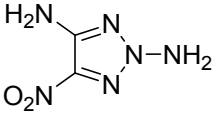
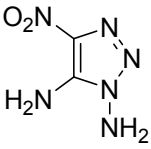
c)

Figure S4 Packing diagram of compound **6** viewed along *a*, *b* and *c*-axes at the 50% probability level.



Scheme S1. Isodesmic reactions

Table S10 Calculated (B3LYP/6-31+G**// MP2/6-311++G**) total energy(E_0), zero-point energy (*ZPE*), Thermal correction to Enthalpy (H_T), HOR (Heat of isodesmic reaction) and heats of formation (HOF) for **1 6.**

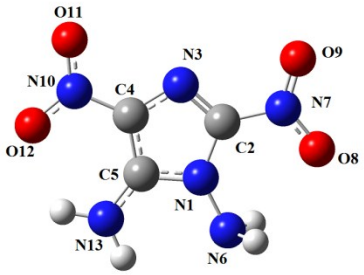
Structure	*ZPE*	H_T	E_0	Corrected E_0	HOR (Hartree/Particle)	ΔHsub (kJ mol^{-1})	HOF (kJ mol^{-1})
	0.05903	0.06357	-241.63672	-241.57551	-	-	267.6[a]
	0.05981	0.06432	-241.64504	-241.58312	-	-	251.8[a]
	0.079945	0.090475	-688.5747224	-688.4874452	0.0888356	-	-114.5
	0.09235	0.103452	-689.0721577	-688.97240	0.0256519	71.1	+48.7
	0.109353	0.121693	-744.2574452	-744.14013	0.04371268	87.1	+124.5
	0.094112	0.103461	-556.15593	-556.0562335	0.04333574	84	+263.0
	0.095357	0.1051	-556.1692086	-556.0679229	0.04741514	91.2	+229.3
	0.094569	0.104601	-556.1638316	-556.0630134	0.05011562	87.0	+242.2

[a] Calculated from G2,

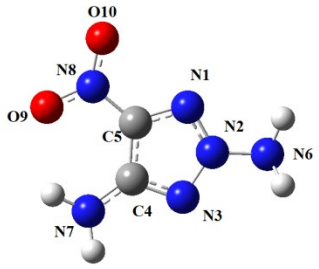
Table S11 Calculated heat of formation for **1**.

Compound	ΔH_L (kJ/mol)	ΔH_f^{Cation} (kJ/mol)	ΔH_f^{Anion} (kJ/mol)	ΔH_f^{298} (kJ/mol)
1	522.3754598	626.4	-114.5	-10.5

Bond Dissociation energy calculation (ub3lyp/6-31+G)**



3



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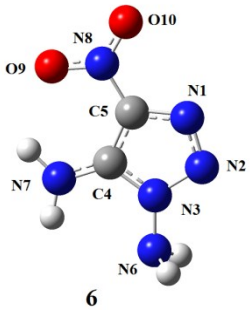

6

Table S12 Bond-dissociation energies of **3**, **5** and **6** (kcal mol^{-1}).

	3	**5**	**6**
N-NH_2	48.9	59.3	59.7
C2-NO_2	65.3	-	-
C4-NH_2	-	113.4	117.9
C4-NO_2	73.4	-	-
C5-NO_2	-	76.2	76.6
C5-NH_2	115.9	-	-

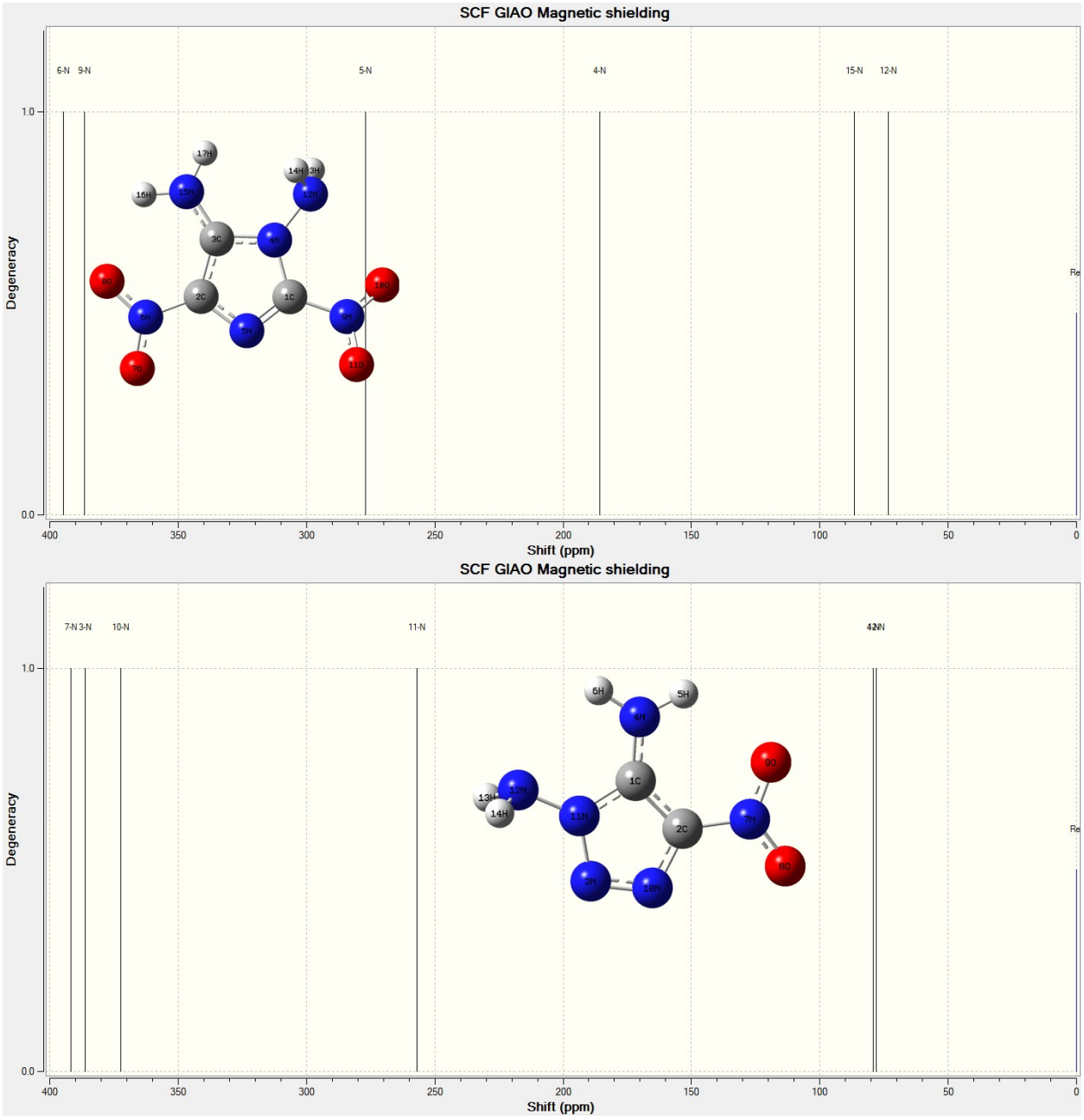

Figure S5. Calculated NMR of compound 3 and 6 by using GIAO (reference to NH_3 B3LYP/6-311+G(2d,p) GIAO)