# Electronic Supplementary Information

## Azo- and methylene-bridged mixed azoles for stable and insensitive energetic applications

Ajay Kumar Chinnam,[a] Qiong Yu,[a] Gregory H. Imler,[b] Damon A. Parrish[b] and Jean'ne M. Shreeve*[a]

[a] Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343 USA.

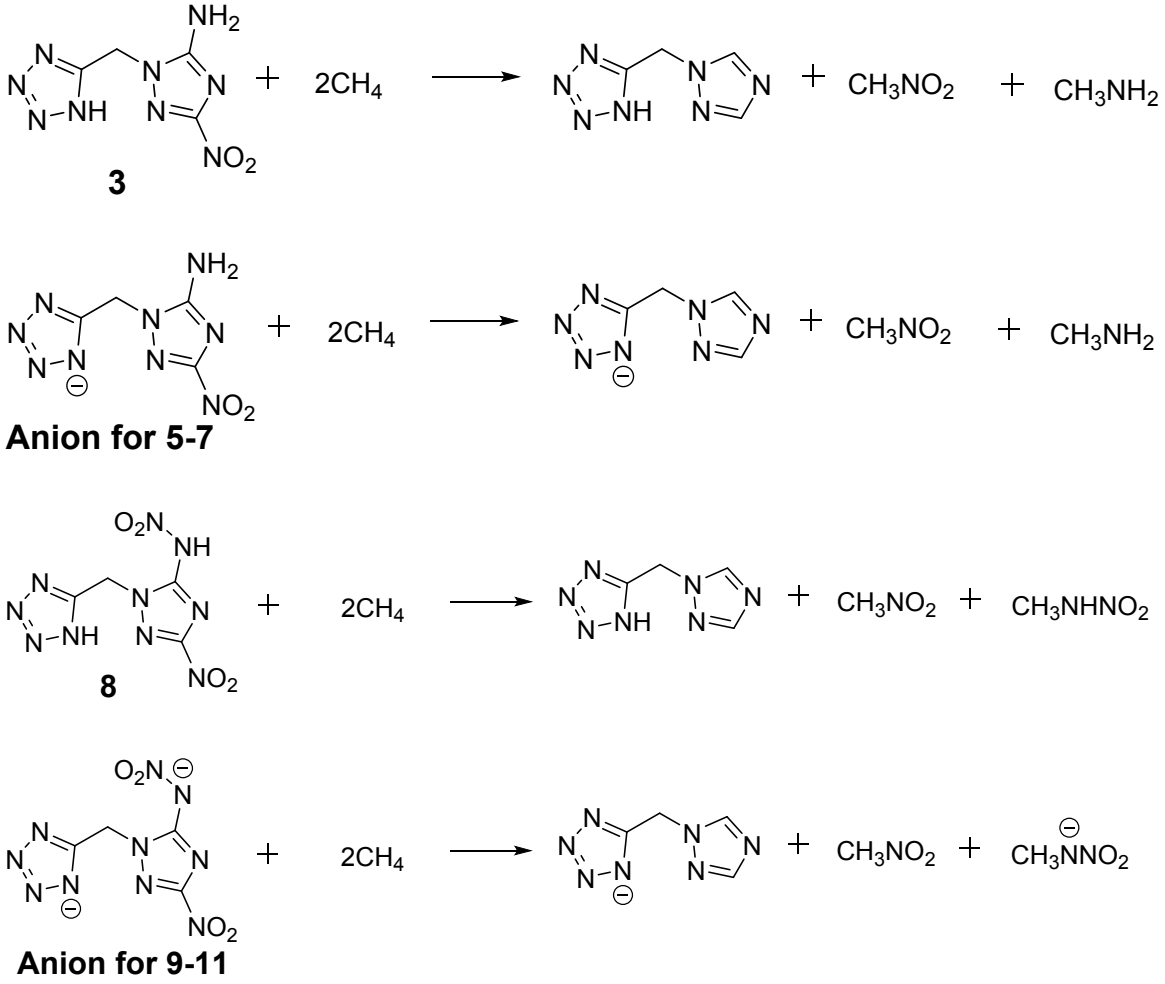
[b] Naval Research Laboratory, 4555 Overlook Avenue, Washington, D.C. 20375 USA

**Table of contents**

## 1. Theoretical calculations

Heats of formation for compounds **3**, **4**, **8** and anions of **5-9**, **9-11** were calculated based on isodesmic reactions (Scheme S1). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[1] The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level. The gas phase enthalpy of formation was calculated, and the enthalpy of reaction was obtained by combining the MP2/6- 311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors.

**Scheme 1**



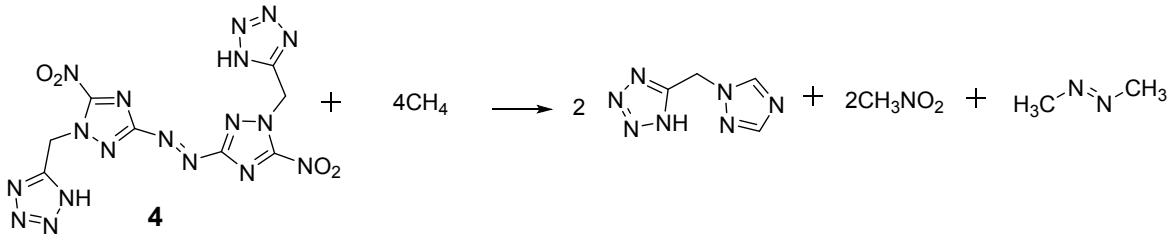



**Table S1** Calculated zero point energy (ZPE), values of the correction (Hr), total energy (E0) and gas-state heats of formation (HOF).[a]

| Compound | ZPE [Hartree /Particle] | HT [Hartree /Particle] | E0 [kJ mol$^{-1}$] | HOF (gas) [kJ mol$^{-1}$] |
|---|---|---|---|---|
| **2** | 0.134645 | 0.147861 | -796.6711541 | 651.83 |
| Anion of **5-7** | 0.121962 | 0.134489 | -796.1815479 | 396.36 |
| **8** | 0.137093 | 0.152560 | -1000.7422053 | 706.71 |
| Anion of **9-11** | 0.110324 | 0.125400 | -999.6214854 | 540.84 |
| **4** | 0.225204 | 0.249977 | -1590.9076155 | 1292.81 |

[a] The enthalpy of sublimation was calculated by using Trouton's rule. Solid-state heats of formation of the resulting compounds were calculated with Equation (1) in which $T_m$ is the melting temperature.

$$\Delta Hf = \Delta Hf(g) - \Delta Hsub = \Delta Hf(g) - 188[J\ mol^{-1}\ K^{-1}] \times T_m \quad (1)$$

## 3. Crystal Structure Data

**Table S2**. Crystal data and structure refinement for **7**.[2-6]

| | | |
|---|---|---|
| CCDC # | 1985501 | |
| Identification code | shrv813 | |
| Empirical formula | $C_4H_8N_{10}O_3$ | |
| Formula weight | 244.20 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 4.2376(3) Å | α= 96.429(3)°. |
| | b = 7.3733(5) Å | β= 94.148(3)°. |
| | c = 15.1316(10) Å | γ = 96.090(3)°. |
| Volume | 465.46(6) $Å^3$ | |
| Z | 2 | |
| Density (-173ºC) | 1.742 $Mg/m^3$ | |
| Density (23ºC) | 1.706 $Mg/m^3$ | |
| Absorption coefficient | 1.292 $mm^{-1}$ | |
| F(000) | 252 | |
| Crystal size | 0.227 x 0.103 x 0.030 $mm^3$ | |
| Theta range for data collection | 2.949 to 74.798°. | |
| Index ranges | -5<=h<=4, -8<=k<=8, -15<=l<=18 | |
| Reflections collected | 3092 | |
| Independent reflections | 1531 [$R_{int}$ = 0.0442] | |
| Completeness to theta = 67.679° | 85.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7538 and 0.5674 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1531 / 0 / 158 | |
| Goodness-of-fit on $F^2$ | 1.070 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0402, $wR_2$ = 0.1059 | |
| R indices (all data) | $R_1$ = 0.0420, $wR_2$ = 0.1090 | |
| Largest diff. peak and hole | 0.226 and -0.293 $e.Å^{-3}$ | |

Single-crystal X-ray structures of **7**

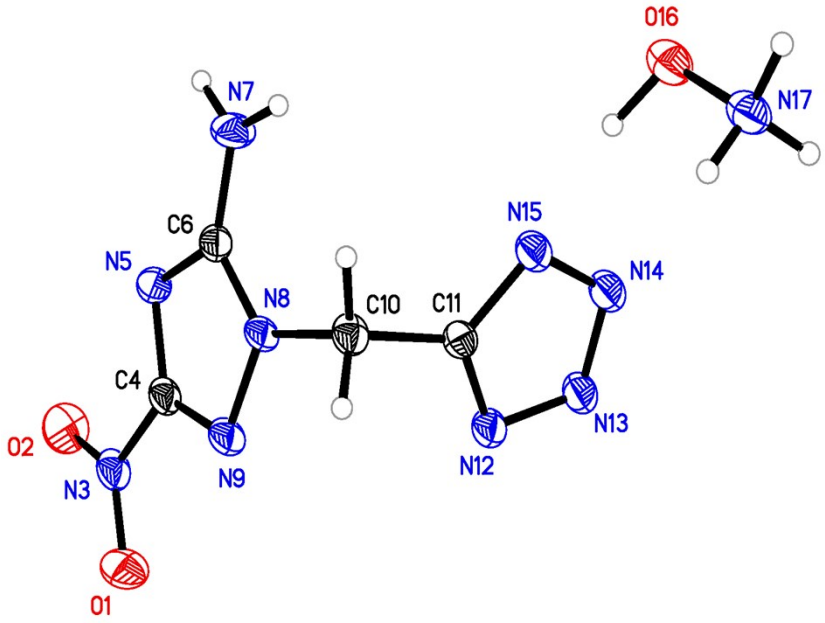



**Figure S1**. Single-crystal X-ray structure of **7** with numbering

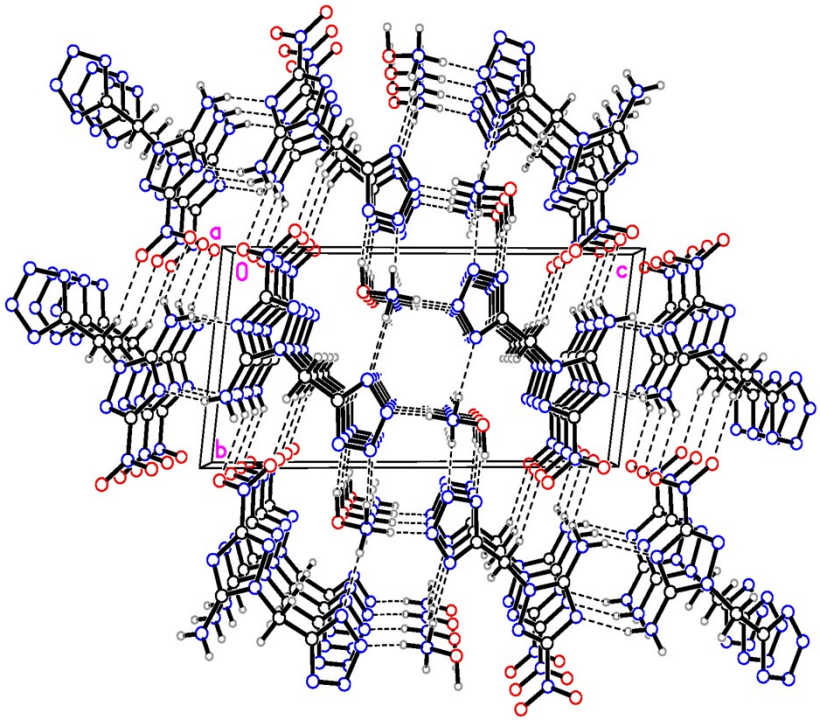



**Figure S2**. Unit cell view of **7** along a axis; hydrogen bonds are marked as dotted lines.

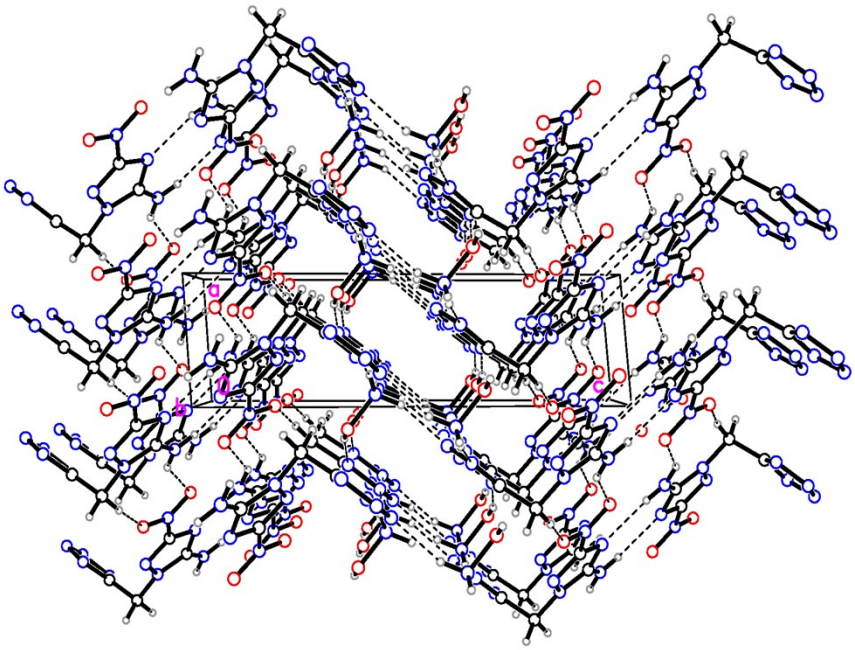



**Figure S3**. Unit cell view of **7** along b axis; hydrogen bonds are marked as dotted lines.

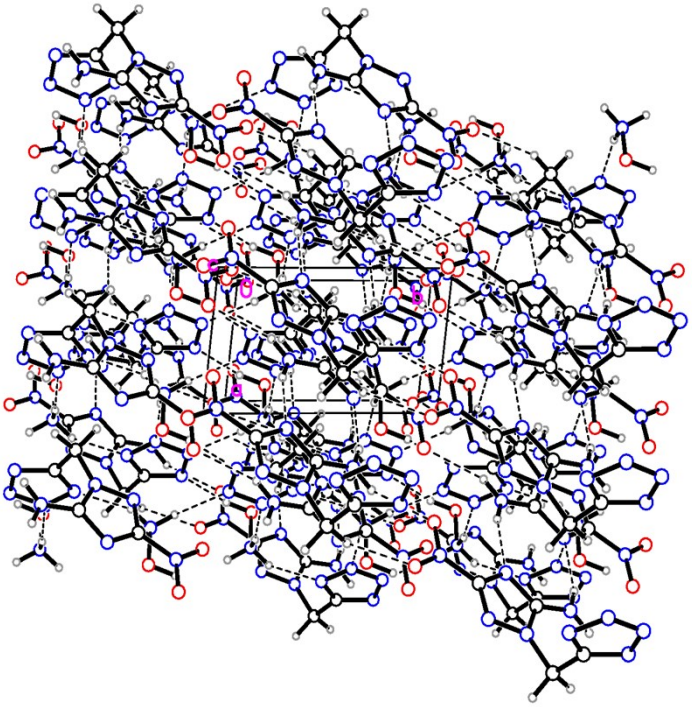


**Figure S4**. Unit cell view of **7** along c axis; hydrogen bonds are marked as dotted lines.

**Table S3**. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for **7**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 9918(3) | 10398(2) | 8150(1) | 39(1) |
| O(2) | 12547(3) | 9670(2) | 9309(1) | 39(1) |
| N(3) | 10469(3) | 9342(2) | 8694(1) | 26(1) |
| C(4) | 8563(4) | 7569(2) | 8599(1) | 21(1) |
| N(5) | 9039(3) | 6366(2) | 9183(1) | 23(1) |
| C(6) | 6852(4) | 4952(2) | 8857(1) | 20(1) |
| N(7) | 6361(4) | 3379(2) | 9200(1) | 30(1) |
| N(8) | 5240(3) | 5390(2) | 8112(1) | 19(1) |
| N(9) | 6375(3) | 7111(2) | 7936(1) | 23(1) |
| C(10) | 2866(3) | 4251(2) | 7479(1) | 21(1) |
| C(11) | 4440(3) | 3251(2) | 6742(1) | 19(1) |
| N(12) | 6134(3) | 4086(2) | 6161(1) | 22(1) |
| N(13) | 7278(3) | 2711(2) | 5664(1) | 24(1) |
| N(14) | 6275(3) | 1137(2) | 5935(1) | 25(1) |
| N(15) | 4455(3) | 1430(2) | 6618(1) | 23(1) |
| O(16) | 1537(3) | -2140(2) | 6508(1) | 31(1) |
| N(17) | -1033(3) | -2318(2) | 5840(1) | 25(1) |

**Table S4**. Bond lengths [Å] and angles [°] for **7**.

| | | | |
|---|---|---|---|
| O(1)-N(3) | 1.221(2) | O(2)-N(3) | 1.2191(19) |
| N(3)-C(4) | 1.4491(19) | C(4)-N(9) | 1.305(2) |
| C(4)-N(5) | 1.340(2) | N(5)-C(6) | 1.3430(19) |
| C(6)-N(7) | 1.326(2) | C(6)-N(8) | 1.362(2) |
| N(7)-H(7A) | 0.8800 | N(7)-H(7B) | 0.8800 |
| N(8)-N(9) | 1.3708(18) | N(8)-C(10) | 1.4618(18) |
| C(10)-C(11) | 1.503(2) | C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 | C(11)-N(12) | 1.336(2) |
| C(11)-N(15) | 1.336(2) | N(12)-N(13) | 1.3471(18) |
| N(13)-N(14) | 1.312(2) | N(14)-N(15) | 1.3458(19) |
| O(16)-N(17) | 1.4163(18) | O(16)-H(16) | 0.95(3) |
| N(17)-H(17A) | 0.9100 | N(17)-H(17B) | 0.9100 |
| N(17)-H(17C) | 0.9100 | | |
| O(2)-N(3)-O(1) | 124.42(14) | O(2)-N(3)-C(4) | 117.44(14) |
| O(1)-N(3)-C(4) | 118.13(14) | N(9)-C(4)-N(5) | 118.97(14) |
| N(9)-C(4)-N(3) | 120.38(15) | N(5)-C(4)-N(3) | 120.65(14) |
| C(4)-N(5)-C(6) | 101.41(13) | N(7)-C(6)-N(5) | 125.42(15) |
| N(7)-C(6)-N(8) | 125.56(14) | N(5)-C(6)-N(8) | 109.02(14) |
| C(6)-N(7)-H(7A) | 120.0 | C(6)-N(7)-H(7B) | 120.0 |
| H(7A)-N(7)-H(7B) | 120.0 | C(6)-N(8)-N(9) | 110.46(12) |
| C(6)-N(8)-C(10) | 129.59(13) | N(9)-N(8)-C(10) | 119.62(13) |
| C(4)-N(9)-N(8) | 100.14(13) | N(8)-C(10)-C(11) | 110.76(12) |
| N(8)-C(10)-H(10A) | 109.5 | C(11)-C(10)-H(10A) | 109.5 |
| N(8)-C(10)-H(10B) | 109.5 | C(11)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 108.1 | N(12)-C(11)-N(15) | 111.86(14) |
| N(12)-C(11)-C(10) | 123.97(13) | N(15)-C(11)-C(10) | 124.07(15) |
| C(11)-N(12)-N(13) | 104.54(13) | N(14)-N(13)-N(12) | 109.45(13) |
| N(13)-N(14)-N(15) | 109.65(12) | C(11)-N(15)-N(14) | 104.49(13) |
| N(17)-O(16)-H(16) | 107.1(14) | O(16)-N(17)-H(17A) | 109.5 |
| O(16)-N(17)-H(17B) | 109.5 | H(17A)-N(17)-H(17B) | 109.5 |
| O(16)-N(17)-H(17C) | 109.5 | H(17A)-N(17)-H(17C) | 109.5 |
| H(17B)-N(17)-H(17C) | 109.5 | | |

**Table S5**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 56(1) | 20(1) | 40(1) | 10(1) | 3(1) | -8(1) |
| O(2) | 40(1) | 31(1) | 41(1) | 0(1) | -5(1) | -15(1) |
| N(3) | 32(1) | 17(1) | 28(1) | -1(1) | 8(1) | -4(1) |
| C(4) | 25(1) | 15(1) | 23(1) | 0(1) | 6(1) | -2(1) |
| N(5) | 28(1) | 17(1) | 22(1) | 2(1) | 4(1) | -4(1) |
| C(6) | 24(1) | 17(1) | 20(1) | 1(1) | 6(1) | -1(1) |
| N(7) | 41(1) | 19(1) | 27(1) | 7(1) | -4(1) | -9(1) |
| N(8) | 24(1) | 12(1) | 21(1) | 2(1) | 4(1) | -3(1) |
| N(9) | 28(1) | 15(1) | 25(1) | 3(1) | 5(1) | -2(1) |
| C(10) | 20(1) | 18(1) | 22(1) | 1(1) | 3(1) | -2(1) |
| C(11) | 21(1) | 16(1) | 20(1) | 2(1) | 0(1) | -1(1) |
| N(12) | 27(1) | 18(1) | 21(1) | 2(1) | 5(1) | -1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N(13) | 29(1) | 19(1) | 25(1) | 0(1) | 5(1) | 0(1) |
| N(14) | 31(1) | 19(1) | 26(1) | 1(1) | 7(1) | 0(1) |
| N(15) | 28(1) | 18(1) | 24(1) | 1(1) | 5(1) | -1(1) |
| O(16) | 36(1) | 21(1) | 34(1) | 4(1) | -1(1) | -3(1) |
| N(17) | 28(1) | 18(1) | 29(1) | 4(1) | 7(1) | 1(1) |

**Table S6**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **7**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(7A) | 7521 | 3198 | 9682 | 36 |
| H(7B) | 4876 | 2515 | 8946 | 36 |
| H(10A) | 1373 | 5036 | 7221 | 25 |
| H(10B) | 1626 | 3349 | 7795 | 25 |
| H(16) | 2310(60) | -870(30) | 6622(16) | 46 |
| H(17A) | -288 | -2513 | 5292 | 37 |
| H(17B) | -1998 | -1270 | 5880 | 37 |

**Table S7**. Torsion angles [°] for **7**.

| | |
|---|---|
| O(2)-N(3)-C(4)-N(9) | -177.63(14) |
| O(1)-N(3)-C(4)-N(9) | 1.5(2) |
| O(2)-N(3)-C(4)-N(5) | 1.7(2) |
| O(1)-N(3)-C(4)-N(5) | -179.19(14) |
| N(9)-C(4)-N(5)-C(6) | -0.44(18) |
| N(3)-C(4)-N(5)-C(6) | -179.79(13) |
| C(4)-N(5)-C(6)-N(7) | 179.51(15) |
| C(4)-N(5)-C(6)-N(8) | 0.02(15) |
| N(7)-C(6)-N(8)-N(9) | -179.13(14) |
| N(5)-C(6)-N(8)-N(9) | 0.36(16) |
| N(7)-C(6)-N(8)-C(10) | -5.9(2) |
| N(5)-C(6)-N(8)-C(10) | 173.61(13) |
| N(5)-C(4)-N(9)-N(8) | 0.64(17) |
| N(3)-C(4)-N(9)-N(8) | 179.99(13) |
| C(6)-N(8)-N(9)-C(4) | -0.57(15) |
| C(10)-N(8)-N(9)-C(4) | -174.59(12) |
| C(6)-N(8)-C(10)-C(11) | -88.86(18) |
| N(9)-N(8)-C(10)-C(11) | 83.86(16) |
| N(8)-C(10)-C(11)-N(12) | -63.1(2) |
| N(8)-C(10)-C(11)-N(15) | 113.17(16) |
| N(15)-C(11)-N(12)-N(13) | -0.81(17) |

| | |
|---|---|
| C(10)-C(11)-N(12)-N(13) | 175.88(13) |
| C(11)-N(12)-N(13)-N(14) | 0.61(16) |
| N(12)-N(13)-N(14)-N(15) | -0.22(17) |
| N(12)-C(11)-N(15)-N(14) | 0.69(17) |
| C(10)-C(11)-N(15)-N(14) | -176.01(13) |
| N(13)-N(14)-N(15)-C(11) | -0.28(17) |

**Table S8**. Hydrogen bonds for **7** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(7)-H(7A)...N(5)#1 | 0.88 | 2.14 | 2.9916(19) | 161.7 |
| N(7)-H(7B)...O(2)#2 | 0.88 | 2.36 | 3.0531(18) | 135.7 |
| O(16)-H(16)...N(15) | 0.95(3) | 1.84(3) | 2.7688(18) | 165(2) |
| N(17)-H(17A)...N(13)#4 | 0.91 | 2.00 | 2.876(2) | 160.9 |
| N(17)-H(17B)...N(14)#5 | 0.91 | 1.99 | 2.8927(19) | 174.6 |
| N(17)-H(17C)...N(12)#2 | 0.91 | 2.05 | 2.899(2) | 155.3 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2 #2 x-1,y-1,z #3 x,y+1,z
#4 -x+1,-y,-z+1 #5 x-1,y,z

**Table S9**. Crystal data and structure refinement for **10**.[7-10]

| | |
|---|---|
| Formula | $C_4H_{12}N_{14}O_4$ |
| CCDC | 1975376 |
| $D_{calc.}$/ g cm$^{-3}$ | 1.709 |
| $\mu$/mm$^{-1}$ | 1.287 |
| Formula Weight | 320.28 |
| Colour | yellow |
| Shape | needle |
| Size/mm$^3$ | 0.37×0.14×0.05 |
| $T$/K | 173(1) |
| Crystal System | monoclinic |
| Space Group | $P2_1/c$ |
| $a$/Å | 8.63810(10) |
| $b$/Å | 13.5120(2) |
| $c$/Å | 10.66810(10) |
| $\alpha$/° | 90 |
| $\beta$/° | 91.2230(10) |
| $\gamma$/° | 90 |
| V/Å$^3$ | 1244.88(3) |
| $Z$ | 4 |
| $Z'$ | 1 |
| Wavelength/Å | 1.541838 |
| Radiation type | $CuK_\alpha$ |
| $\theta_{min}$/° | 5.121 |
| $\theta_{max}$/° | 68.400 |
| Measured Refl. | 10664 |
| Independent Refl. | 2288 |
| Reflections with I > 2(I) | 1956 |
| $R_{int}$ | 0.0367 |
| Parameters | 247 |
| Restraints | 0 |
| Largest Peak | 0.229 |
| Deepest Hole | -0.253 |
| GooF | 1.041 |
| $wR_2$ (all data) | 0.0885 |
| $wR_2$ | 0.0837 |
| $R_1$ (all data) | 0.0401 |
| $R_1$ | 0.0331 |

Single-crystal X-ray structures of **10**

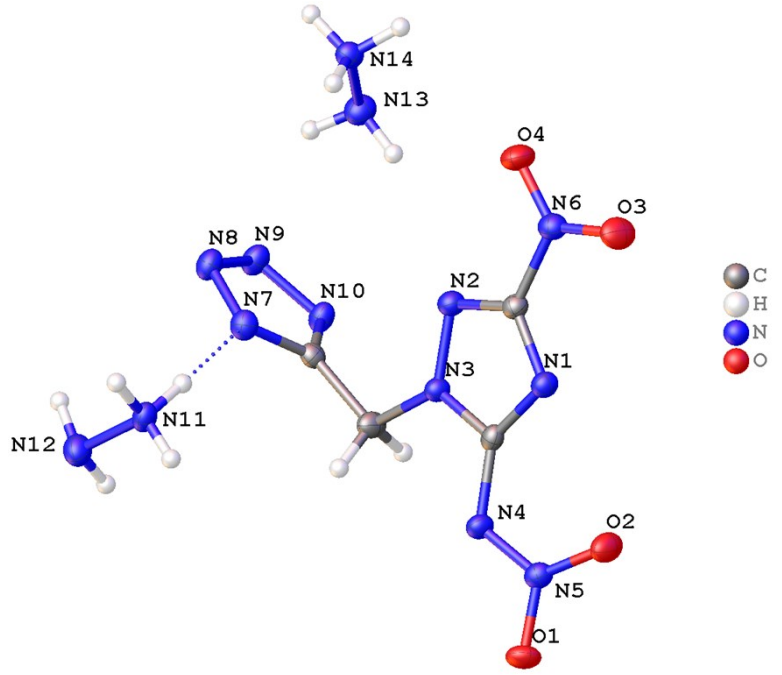



**Figure S5.** Single-crystal X-ray structure of **10** with numbering.

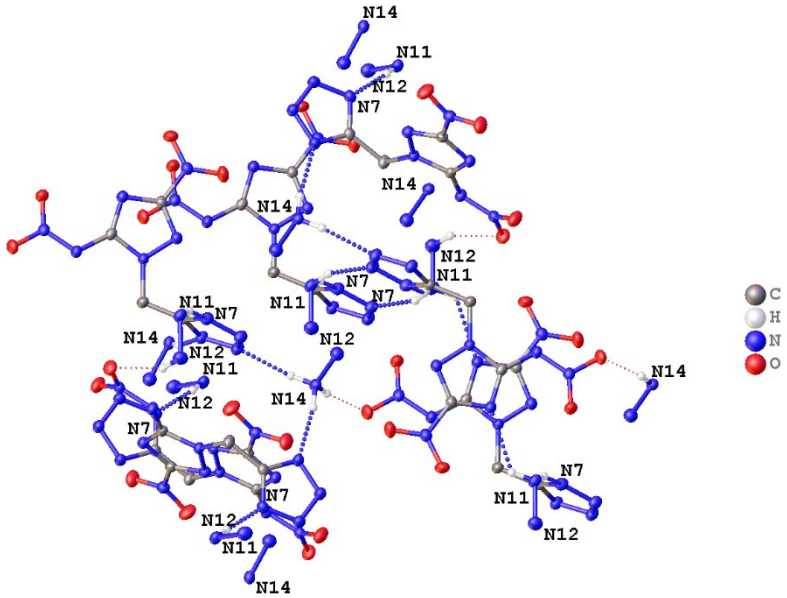



**Figure S6.** The following hydrogen bonding interactions with a maximum D-D distance of 3.1 Å and a minimum angle of 110 ° are present in **10**: N14–O1_*1: 2.848 Å, N14–O3*_2: 2.888 Å, N14–N10_*3: 2.919 Å, N14–N9*_4: 2.902 Å, N11–N1_*1: 2.976 Å, N11–N7: 2.873 Å, N11–N8*_5: 2.879 Å, N12–O1_*6: 3.075 Å.*

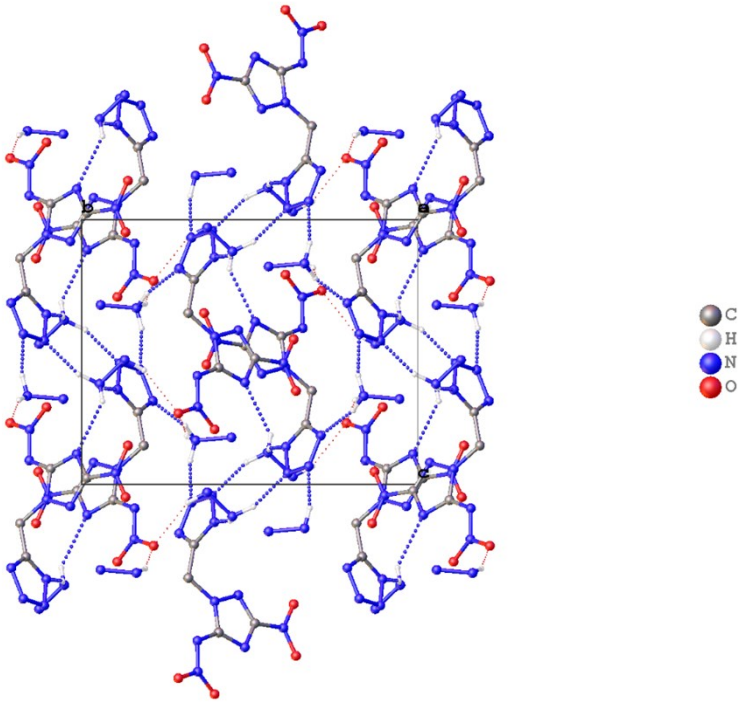



**Figure S7.** Packing diagram of **10**.

**Table S10.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalized $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| O1 | 6791.1(12) | 7132.0(8) | 7316.2(11) | 24.5(3) |
| O2 | 5087.4(14) | 6054.4(9) | 7918.0(10) | 28.3(3) |
| O3 | 1331.9(14) | 3633.5(9) | 6468.7(11) | 29.1(3) |
| O4 | 567.2(14) | 3702.1(9) | 4521.2(11) | 30.5(3) |
| N3 | 3338.0(14) | 6051.7(9) | 4422.5(11) | 16.1(3) |
| N1 | 3315.3(15) | 5154.0(9) | 6147.7(12) | 18.2(3) |
| N14 | 245.2(16) | 3380.7(10) | 1659.6(13) | 18.7(3) |
| N2 | 2259.8(14) | 5348.2(9) | 4178.5(12) | 18.2(3) |
| N5 | 5663.2(14) | 6555.0(9) | 7070.8(12) | 17.9(3) |
| N10 | 1724.1(14) | 7104.2(10) | 1847.4(12) | 19.6(3) |
| N7 | 3611.9(15) | 6063.4(10) | 1420.1(12) | 20.3(3) |
| N6 | 1336.5(15) | 4003.4(10) | 5417.0(12) | 20.1(3) |
| N11 | 6813.7(16) | 5527.7(10) | 1203.9(12) | 20.0(3) |
| N8 | 2630.7(15) | 6124.6(10) | 430.1(12) | 20.9(3) |
| N9 | 1507.7(15) | 6745.8(10) | 686.0(12) | 21.4(3) |
| N4 | 5158.8(14) | 6566.5(10) | 5902.1(12) | 18.6(3) |
| N12 | 7227.7(17) | 6272.9(11) | 298.0(14) | 25.7(3) |
| N13 | 118.4(17) | 4445.7(10) | 1775.8(15) | 25.1(3) |
| C4 | 3020.7(16) | 6665.4(11) | 2269.9(14) | 16.3(3) |
| C2 | 2321.9(17) | 4856.8(11) | 5241.2(13) | 16.7(3) |
| C1 | 3970.3(16) | 5932.0(11) | 5590.7(13) | 16.3(3) |
| C3 | 3737.4(19) | 6836.8(12) | 3531.1(14) | 20.9(3) |

**Table S11.** Anisotropic Displacement Parameters (×$10^4$) **10**. The anisotropic displacement factor exponent takes the form: -2□$^2$[$h^2a^{*2} \times U_{11}$+ ... +2hka* × b* × $U_{12}$]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O1 | 19.6(5) | 25.9(6) | 27.6(6) | -0.3(5) | -7.1(4) | -5.8(5) |
| O2 | 38.4(7) | 27.9(6) | 18.5(6) | 4.1(5) | -3.5(5) | -9.8(5) |
| O3 | 37.0(7) | 25.0(6) | 25.1(6) | 9.3(5) | -3.9(5) | -7.4(5) |
| O4 | 32.8(6) | 33.3(7) | 25.2(6) | -4.6(5) | -3.6(5) | -12.7(5) |
| N3 | 16.8(6) | 16.4(6) | 15.1(6) | 0.8(5) | -1.6(5) | -0.6(5) |
| N1 | 19.6(6) | 18.5(6) | 16.5(6) | 0.3(5) | -1.5(5) | 0.0(5) |
| N14 | 18.0(7) | 19.7(7) | 18.3(7) | 2.6(5) | -1.9(5) | -0.6(5) |
| N2 | 18.7(6) | 17.8(6) | 18.1(6) | -0.9(5) | -0.9(5) | -1.0(5) |
| N5 | 17.6(6) | 16.7(6) | 19.2(6) | -0.6(5) | -2.1(5) | 2.1(5) |
| N10 | 21.4(6) | 21.8(7) | 15.6(6) | -0.8(5) | -0.4(5) | 4.2(5) |
| N7 | 21.0(6) | 19.4(7) | 20.4(7) | 1.0(5) | 1.1(5) | 3.6(5) |
| N6 | 20.3(6) | 18.2(7) | 21.8(7) | -1.4(5) | -0.3(5) | -0.6(5) |
| N11 | 20.4(7) | 24.9(7) | 14.7(6) | 0.0(5) | 0.4(5) | 2.4(5) |
| N8 | 25.0(7) | 20.8(7) | 16.8(6) | -1.1(5) | 0.6(5) | 3.8(5) |
| N9 | 23.3(7) | 23.5(7) | 17.2(6) | -1.1(5) | -2.0(5) | 4.3(5) |
| N4 | 19.2(6) | 20.2(7) | 16.4(6) | 0.3(5) | -2.8(5) | -2.1(5) |
| N12 | 30.4(8) | 24.5(8) | 22.5(7) | 0.7(6) | 4.5(6) | -2.7(6) |
| N13 | 29.8(7) | 21.5(7) | 24.0(7) | -0.4(6) | -1.0(6) | -0.6(6) |
| C4 | 16.5(7) | 15.1(7) | 17.5(7) | 2.9(6) | 1.1(6) | -0.8(5) |
| C2 | 17.4(7) | 15.9(7) | 16.9(7) | -1.4(6) | 0.1(6) | 0.2(6) |
| C1 | 16.2(7) | 18.8(7) | 13.7(7) | -1.2(6) | 0.6(5) | 2.9(6) |
| C3 | 24.4(8) | 20.3(8) | 18.0(8) | 3.8(6) | -3.1(6) | -4.3(6) |

**Table S12.** Bond Lengths in Å for **10**.

| Atom | Atom | Length/Å |
|---|---|---|
| O1 | N5 | 1.2707(17) |
| O2 | N5 | 1.2414(17) |
| O3 | N6 | 1.2283(17) |
| O4 | N6 | 1.2220(17) |
| N3 | N2 | 1.3523(18) |
| N3 | C1 | 1.3596(18) |
| N3 | C3 | 1.4706(19) |
| N1 | C2 | 1.3406(19) |
| N1 | C1 | 1.339(2) |
| N14 | N13 | 1.4487(19) |
| N2 | C2 | 1.314(2) |
| N5 | N4 | 1.3121(18) |
| N10 | N9 | 1.3396(18) |
| N10 | C4 | 1.3370(19) |
| N7 | N8 | 1.3426(18) |
| N7 | C4 | 1.328(2) |
| N6 | C2 | 1.448(2) |
| N11 | N12 | 1.4458(19) |
| N8 | N9 | 1.3158(19) |
| N4 | C1 | 1.3729(19) |
| C4 | C3 | 1.487(2) |

**Table S13.** Bond Angles in ° for **10**.

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| N2 | N3 | C1 | 110.75(12) |
| N2 | N3 | C3 | 123.56(12) |
| C1 | N3 | C3 | 125.69(12) |
| C1 | N1 | C2 | 100.66(12) |
| C2 | N2 | N3 | 100.01(12) |
| O1 | N5 | N4 | 115.22(12) |
| O2 | N5 | O1 | 120.11(12) |
| O2 | N5 | N4 | 124.62(13) |
| C4 | N10 | N9 | 104.53(12) |
| C4 | N7 | N8 | 104.70(12) |
| O3 | N6 | C2 | 117.11(13) |
| O4 | N6 | O3 | 124.50(14) |
| O4 | N6 | C2 | 118.39(13) |
| N9 | N8 | N7 | 109.38(12) |
| N8 | N9 | N10 | 109.49(12) |
| N5 | N4 | C1 | 117.00(12) |
| N10 | C4 | C3 | 124.44(14) |
| N7 | C4 | N10 | 111.90(13) |
| N7 | C4 | C3 | 123.66(14) |
| N1 | C2 | N6 | 120.94(13) |
| N2 | C2 | N1 | 119.00(14) |
| N2 | C2 | N6 | 120.06(13) |
| N3 | C1 | N4 | 115.54(13) |
| N1 | C1 | N3 | 109.57(13) |
| N1 | C1 | N4 | 134.74(14) |
| N3 | C3 | C4 | 111.95(12) |

**Table S14.** Torsion Angles in ° for **10**.

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| O1 | N5 | N4 | C1 | 178.16(12) |
| O2 | N5 | N4 | C1 | -4.1(2) |
| O3 | N6 | C2 | N1 | 7.6(2) |
| O3 | N6 | C2 | N2 | -72.96(14) |
| O4 | N6 | C2 | N1 | -72.67(14) |
| O4 | N6 | C2 | N2 | 6.8(2) |
| N3 | N2 | C2 | N1 | -0.21(17) |
| N3 | N2 | C2 | N6 | -79.70(12) |
| N2 | N3 | C1 | N1 | -0.57(16) |
| N2 | N3 | C1 | N4 | 175.59(12) |
| N2 | N3 | C3 | C4 | -9.7(2) |
| N5 | N4 | C1 | N3 | 171.68(12) |
| N5 | N4 | C1 | N1 | -13.4(2) |
| N10 | C4 | C3 | N3 | 99.03(17) |
| N7 | N8 | N9 | N10 | -0.11(17) |
| N7 | C4 | C3 | N3 | -81.91(18) |
| N8 | N7 | C4 | N10 | -0.56(16) |
| N8 | N7 | C4 | C3 | -79.72(13) |
| N9 | N10 | C4 | N7 | 0.50(17) |
| N9 | N10 | C4 | C3 | 179.65(14) |

| Atom | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|
| C4 | N10 | N9 | N8 | -0.23(16) |
| C4 | N7 | N8 | N9 | 0.40(16) |
| C2 | N1 | C1 | N3 | 0.39(15) |
| C2 | N1 | C1 | N4 | -74.73(16) |
| C1 | N3 | N2 | C2 | 0.45(15) |
| C1 | N3 | C3 | C4 | 170.98(13) |
| C1 | N1 | C2 | N2 | -0.12(18) |
| C1 | N1 | C2 | N6 | 179.37(13) |
| C3 | N3 | N2 | C2 | -79.00(13) |
| C3 | N3 | C1 | N1 | 178.87(13) |
| C3 | N3 | C1 | N4 | -5.0(2) |

**Table S15.** Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **10**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$.

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H11A | 7030(20) | 4898(16) | 840(20) | 37(6) |
| H13A | 650(20) | 4698(16) | 1210(20) | 32(5) |
| H11B | 5790(20) | 5580(14) | 1365(17) | 22(5) |
| H14A | -80(20) | 3221(13) | 894(18) | 19(4) |
| H14B | -390(20) | 3067(15) | 2206(19) | 30(5) |
| H14C | 1210(20) | 3124(15) | 1820(18) | 28(5) |
| H12A | 7060(30) | 6849(19) | 680(20) | 48(7) |
| H13B | 560(20) | 4593(15) | 2510(20) | 31(5) |
| H12B | 6480(20) | 6205(15) | -320(20) | 31(5) |
| H3A | 4840(20) | 6856(15) | 3486(18) | 30(5) |
| H3B | 3390(20) | 7439(15) | 3888(17) | 24(5) |
| H11C | 7330(20) | 5614(16) | 1860(20) | 35(6) |

**Table S16.** Hydrogen Bond information for **10**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/deg |
|---|---|---|---|---|---|---|
| N11 | H11A | N8[1] | 0.95(2) | 1.96(2) | 2.8790(19) | 160.3(18) |
| N11 | H11B | N7 | 0.91(2) | 1.99(2) | 2.8729(19) | 162.8(17) |
| N14 | H14A | N9[2] | 0.885(19) | 2.067(19) | 2.9020(18) | 156.9(16) |
| N14 | H14B | N10[3] | 0.91(2) | 2.02(2) | 2.9191(18) | 166.9(18) |
| N14 | H14C | O1[4] | 0.91(2) | 1.97(2) | 2.8475(17) | 159.9(18) |
| N14 | H14C | O3[5] | 0.91(2) | 2.41(2) | 2.8875(18) | 112.9(15) |
| N12 | H12A | O1[6] | 0.89(3) | 2.24(3) | 3.0753(19) | 156(2) |
| N11 | H11C | N1[4] | 0.83(2) | 2.44(2) | 2.9760(18) | 122.8(18) |

–

[1]1-x,1-y,-z; [2]-x,1-y,-z; [3]-x,-1/2+y,1/2-z; [4]1-x,1-y,1-z; [5]+x,1/2-y,-1/2+z; [6]+x,3/2-y,-1/2+

## 3. DSC Curves

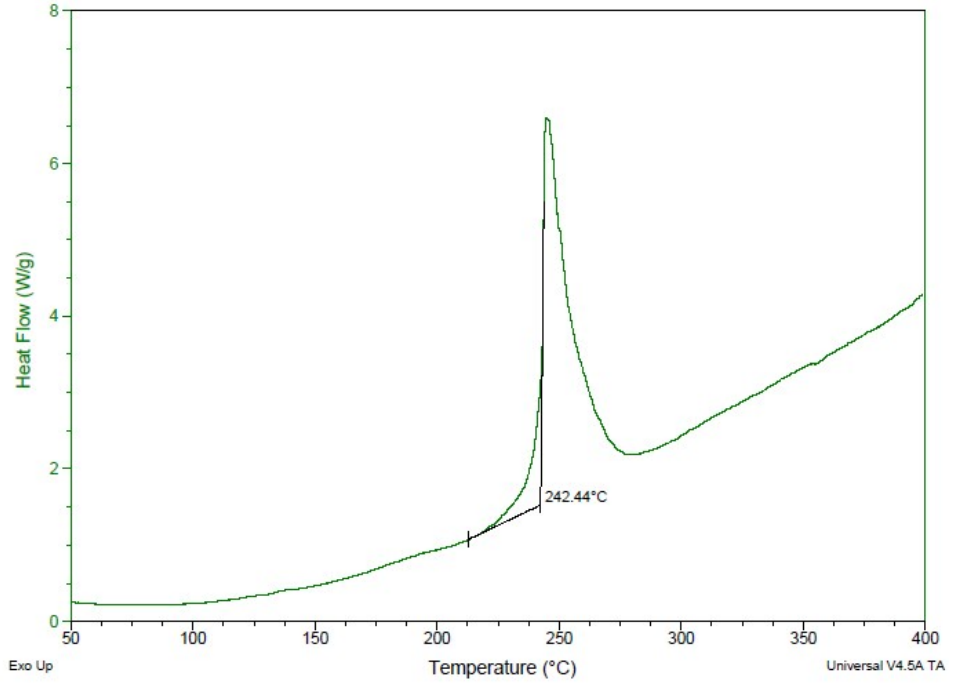



**Figure S8. DSC Curve of 3**

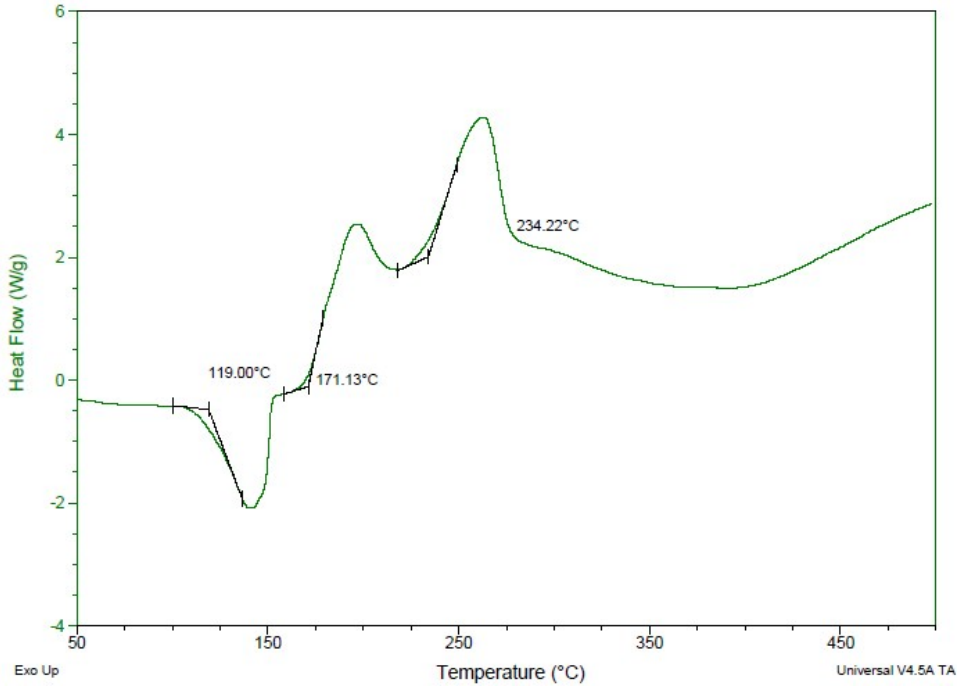



**Figure S9. DSC Curve of 4**

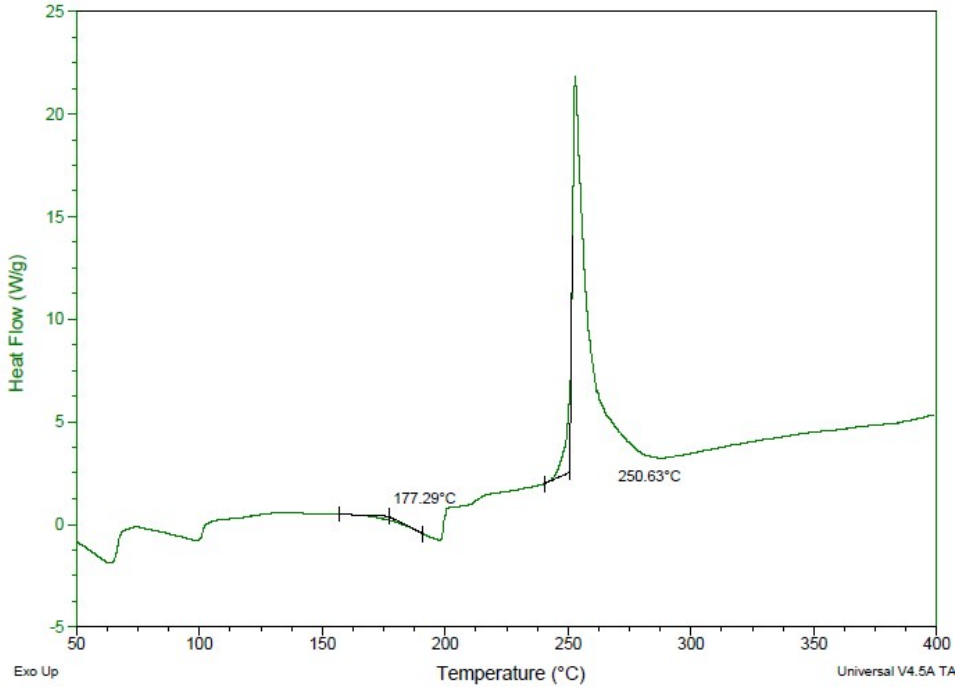



**Figure S10. DSC Curve of 5**

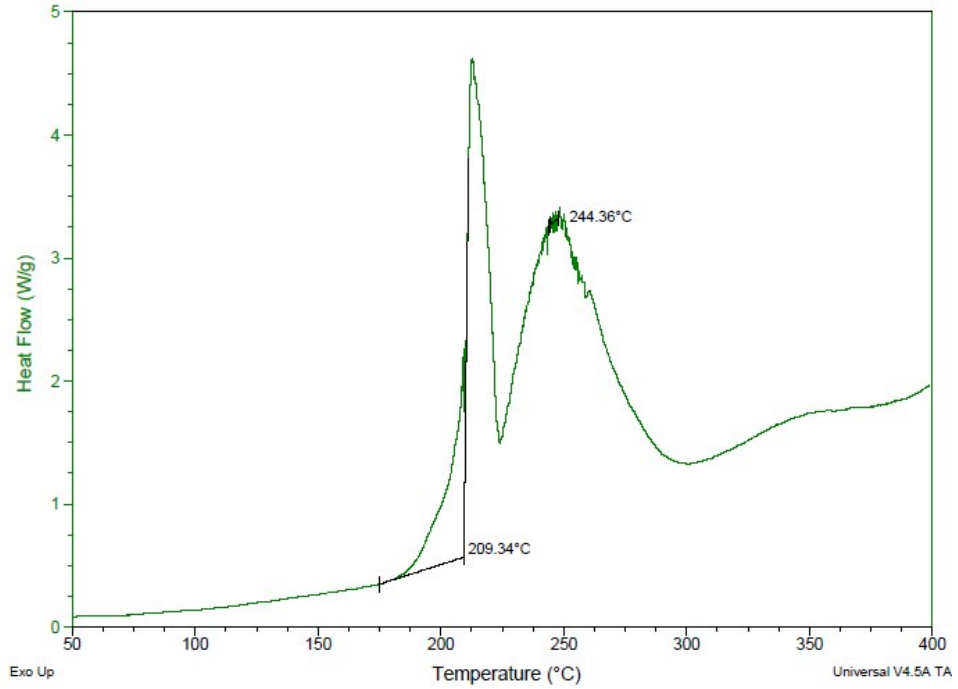



**Figure S11. DSC Curve of 6**

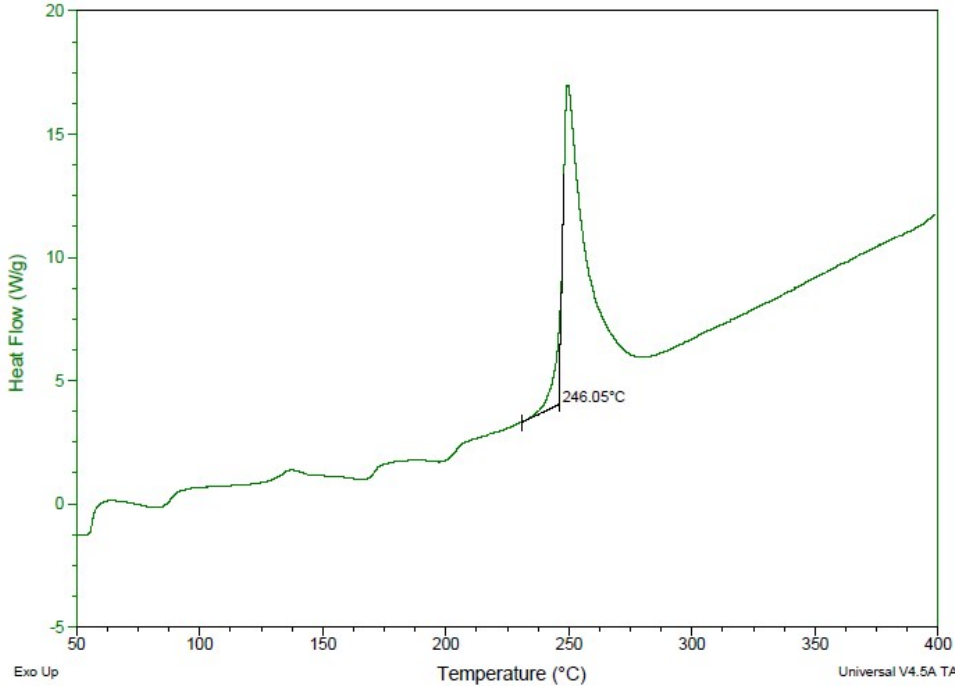



**Figure S12. DSC Curve of 7**

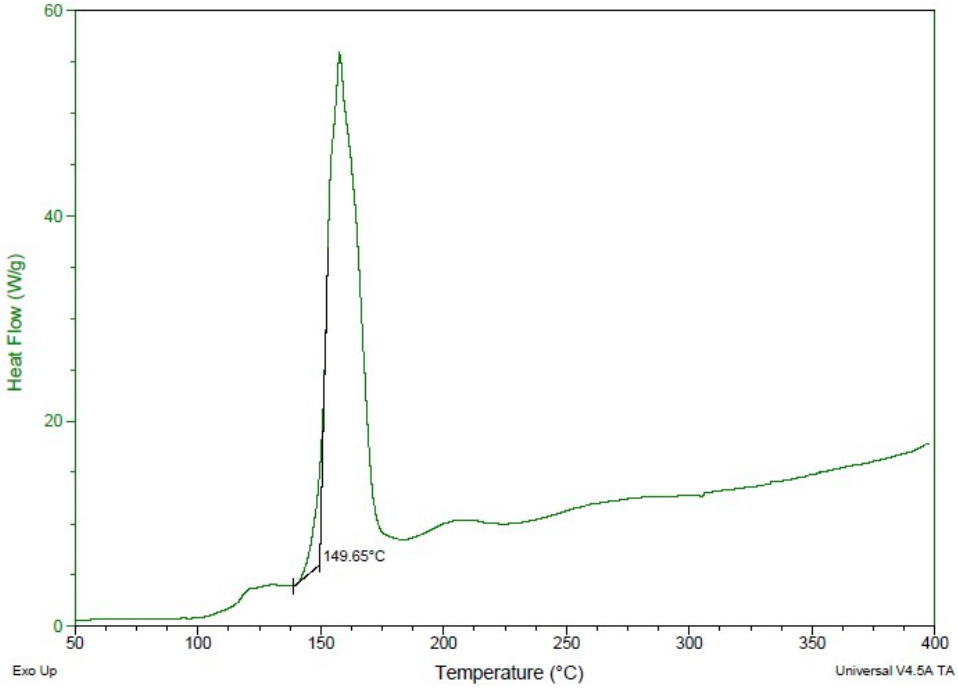



**Figure S13. DSC Curve of 8**

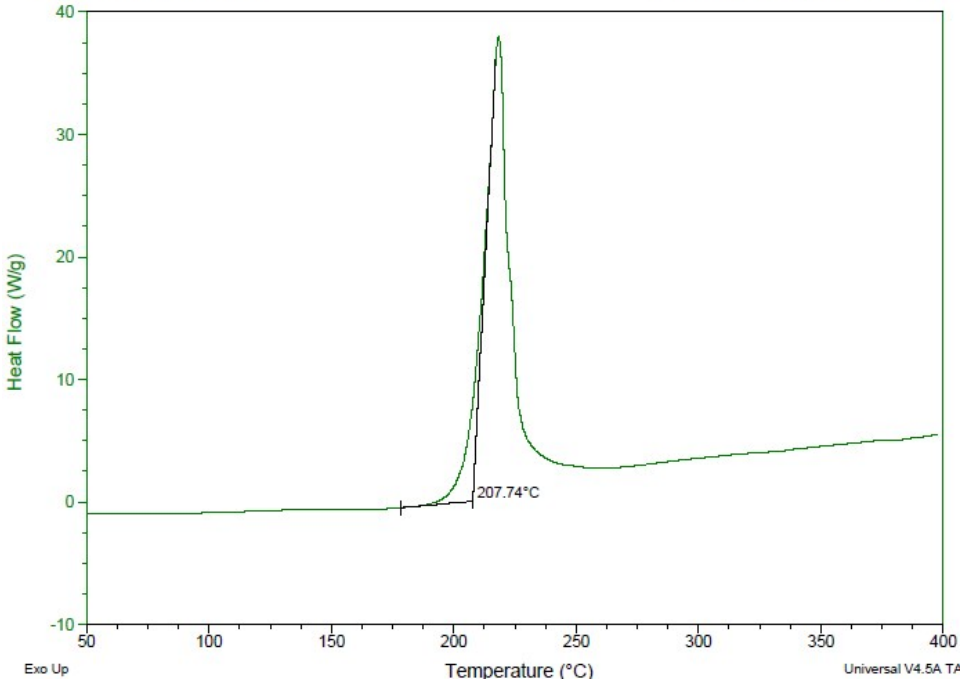



**Figure S14. DSC Curve of 9**

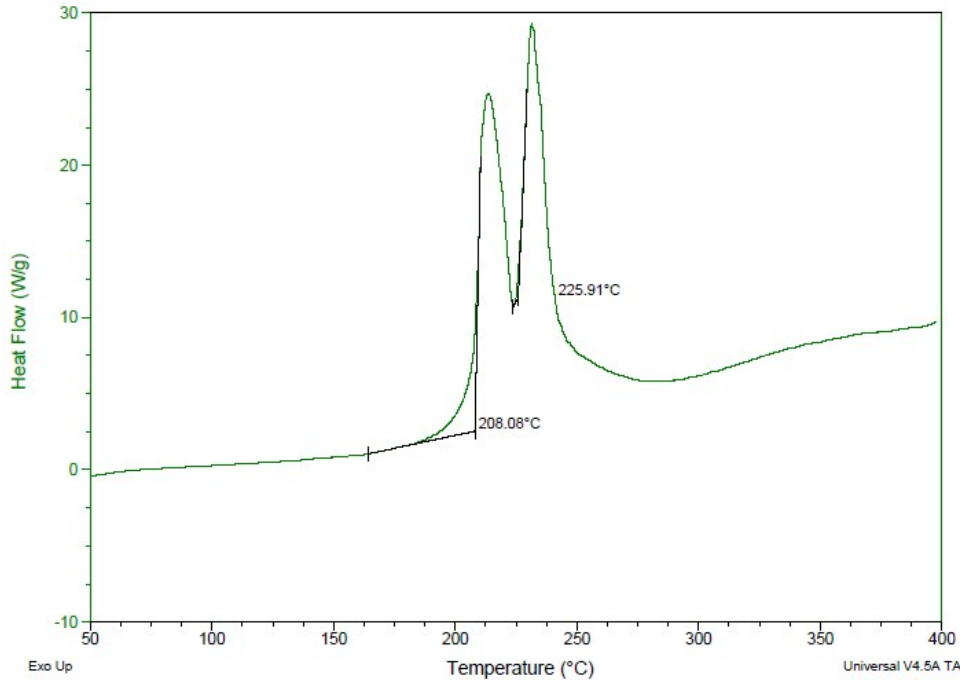



**Figure S15. DSC Curve of 10**

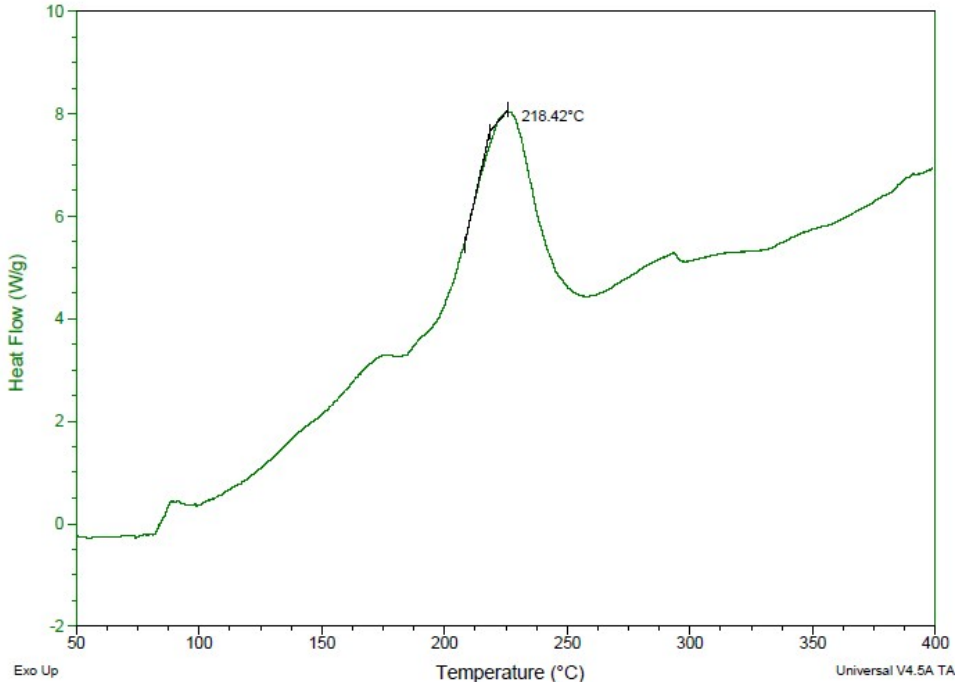



**Figure S16. DSC Curve of 11**

## 4. References


1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson,W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision E.01)*, Gaussian, Inc., Wallingford CT, 2004.
2. Bruker (2015). APEX3 v2015.5-2. Bruker AXS Inc., Madison, Wisconsin, USA.
3. Bruker (2013). SAINT v8.34A. Bruker AXS Inc., Madison, Wisconsin, USA.
4. Bruker (2014). XPREP v2014/2. Bruker AXS Inc., Madison, Wisconsin, USA.
5. Bruker (2014). SADABS v2014/5, Bruker AXS Inc., Madison, Wisconsin, USA.
6. G. M. Sheldrick, (2014). SHELXL-2014/7. University of Göttingen, Germany.

7. COSMO-V1.61 - Software for the CCD Detector Systems for Determining Data Collection Parameters, Bruker axs, Madison, WI (2000).
8. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, 2009, **42**, 339-341.
9. G. M. Sheldrick, Short history of ShelX, *Acta Cryst.*, 2008, **A64**, 339-341.
10. Software for the Integration of CCD Detector System Bruker Analytical X-ray Systems, Bruker axs, Madison, WI (after **2013**).