Electronic Supplementary Information

Multipurpose [1,2,4]Triazolo[4,3-b][1,2,4,5] Tetrazine-based Energetic Materials

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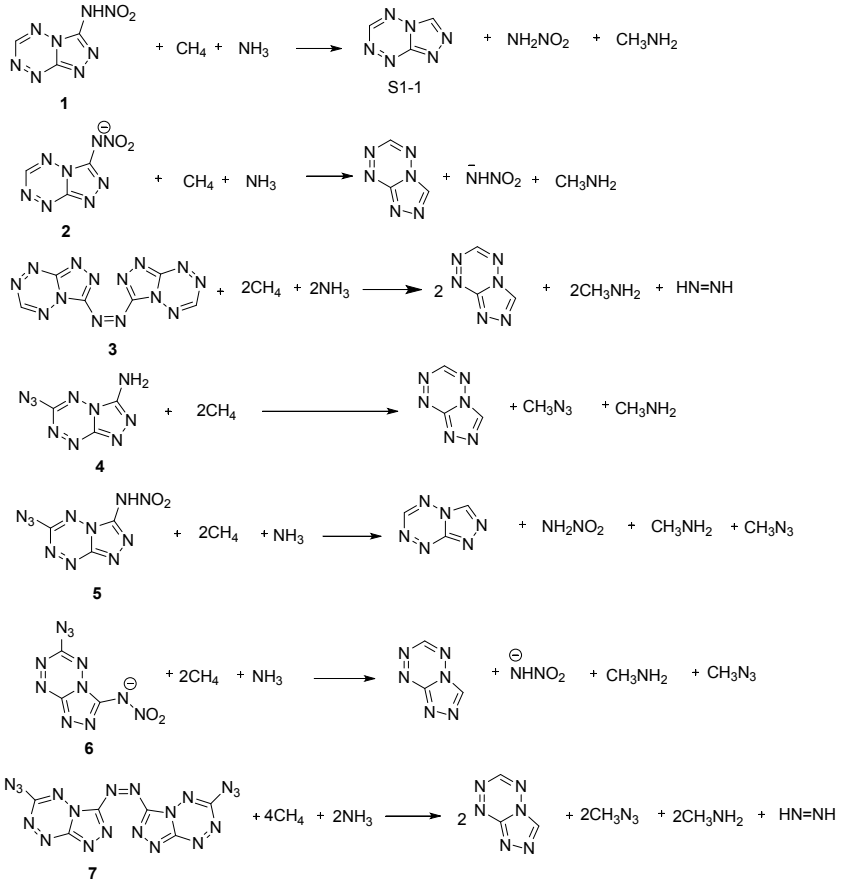
Theoretical calculations

The calculations of the heats of formation were carried out using Gaussian 03 (Revision D.01) suite of programs. All the compounds were determined using isodesmic reactions (Scheme S1). The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level. The gas phase enthalpy of formation was computed 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 S1. isodesmic reactions

Table S1. Calculated zero point energy (*ZPE*), values of the correction (*H*r), total energy (*E*0) and heats of formation (*HOF*)

Species	*ZPE*	*H*r	*E*0	corrected *E*0	*HOF*(kJ mol^{-1})
1	0.08787	0.09815	-702.1648128	-702.07018	647.8152481
2	0.074617	0.084545	-701.6549742	-701.57341	599.0307247
3	0.126185	0.140717	-993.7374837	-993.60181	1525.155442
4	0.088031	0.098805	-661.3370986	-661.24181	913.6448503
5	0.090837	0.103794	-865.3874277	-865.28727	951.8387720
6	0.077009	0.089863	-864.8990836	-864.81230	923.7713178
7	0.131557	0.151424	-1320.226924	-1320.08076	2194.6478964

S1-1	0.06872	0.075225	-442.8562364	-442.78376	682.5926183
CH_4	0.044793	0.048605	-40.3796224	-40.33281	-74.6
NH_3	0.034384	0.038203	-56.4154647	-56.37864	-45.9
NH_2NO_2	0.039257	0.043909	-260.4931748	-260.45084	-6.11
CH_3NH_2	0.06403	0.06840	-95.59384	-95.52800	-23.0
$^-NHNO_2$	0.026168	0.030444	-259.936099	-259.90670	-6.74
HN=NH	0.028443	0.032244	-110.3840486	-110.35294	200.4
CH_3N_3	0.05025	0.05567	-203.60786	-203.55402	296.54

[a] Data obtained from G2.

[b] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.].

Table S2. Calculated solid state heat of formation (*HOF*)

Compound	$\triangle H_L$ (kJ mol^{-1})	$\triangle H_f^{Cation}$ (kJ mol^{-1})	$\triangle H_f^{Anion}$ (kJ mol^{-1})	$\triangle H_f$ (kJ mol^{-1})
4	520.4019634	626.4	599.0307247	705.0287613
5	513.3329922	669.5	599.0307247	755.1977325
6	510.6371394	770.0	599.0307247	858.3935853
8	496.3410163	575.9	599.0307247	678.5897084
9	472.9696499	883.6	599.0307247	1009.661075
15	494.5431588	626.4	923.7713178	1055.628159
16	486.9679653	669.5	923.7713178	1106.303352
17	473.6503792	575.9	923.7713178	1026.020939
18	454.8089406	883.6	923.7713178	1352.562377

X-ray Crystallography of 3, 5, 13, 14 and 17

Table S3. Crystal data and structure refinement for crystals

Compound	**3**	**5**	**13**	**14**	**17**
CCDC number	1884779	1884783	1884785	1884780	1884784
Empirical formula	$C_3H_2N_8O_2$	$C_3H_5N_9O_3$	$C_3H_2N_{10}$	$C_3HN_{11}O_2$	$C_3H_4N_{12}O_3$
Formula weight	182.13	215.16	178.15	223.15	256.18
Temperature	296(2) K	296(2) K	296(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	Cc	$P2_12_12_1$	$P2_1$	$P2_1$
a/Å	6.9340(2)	16.224(2)	5.5258(4)	5.5608(5)	7.7496(12)
b/Å	12.4025(4)	5.5034(7)	6.7155(5)	18.9684(18)	7.7496(12)
c/Å	15.5088(4)	10.7701(13)	18.0885(14)	7.5833(7)	12.611(2)
α/°	90°.	90	90	90	90
β/°	90°.	125.781(3)	90	90.458(2)	98.872(5)
γ/°	90°.	90	90	90	90
Volume	1333.74(7) Å3	780.15(17) Å3	671.24(9) Å3	799.86(13) Å3	476.05(13) Å3
Z	8	4	4	4	2

Density (20°C)	1.814 Mg/m^3	1.832 Mg/m^3	1.763 Mg/m^3	1.853 Mg/m^3	1.787 Mg/m^3
μ/mm-1	0.154	0.160	0.138	0.158	0.155
F(000)	736	440	360	448	260
Crystal size mm3	0.316 x 0.117 x 0.075	0.121 x 0.108 x 0.040	0.219 x 0.195 x 0.020	0.275 x 0.140 x 0.052	0.592 x 0.076 x 0.030
Theta range for data collection/°	2.103 to 30.025	3.095 to 30.068	2.252 to 30.082	2.147 to 29.898	2.900 to 29.983
Index ranges	-9<=h<=9,	-22<=h<=22,	-7<=h<=6,	-7<=h<=7,	-8<=h<=10,
	-15<=k<=17,	-7<=k<=6,	-9<=k<=9,	-23<=k<=26,	-6<=k<=6,
	-21<=l<=21	-15<=l<=15	-25<=l<=25	-10<=l<=10	-17<=l<=17
Reflections collected	14964	4410	7923	9411	5552
Independent reflections	3793 [R_{int} = 0.0267]	2145 [R_{int} = 0.0184]	1927 [R_{int} = 0.0193]	4137 [R_{int} = 0.0209]	2604 [R_{int} = 0.0275]
Data / restraints / parameters	3793 /1 / 235	2145 / 3 / 140	1927 / 0 / 124	4137 / 1 / 289	2604 / 2 /167
Goodness-of-fit on F2	1.032	1.045	1.057	1.091	1.005
Final R indices [I>2sigma(I)]	R_1 = 0.0298, wR_2 = 0.0679	R_1 = 0.0366, wR_2 = 0.0876	R_1 = 0.0296, wR_2 = 0.0726	R_1 = 0.0437, wR_2 = 0.1091	R_1 = 0.0401, wR_2 = 0.0788
R indices (all data)	R_1 = 0.0395, wR_2 = 0.0719	R_1 = 0.0441, wR_2 = 0.0922	R_1 = 0.0356, wR_2 = 0.0754	R_1 = 0.0507, wR_2 = 0.1123	R_1 = 0.0682, wR_2 = 0.0898
Largest diff. peak and hole/e.Å-3	0.157 and -0.161	0.391 and -0.263	0.208 and -0.170	0.223 and -0.239	0.272 and -0.175

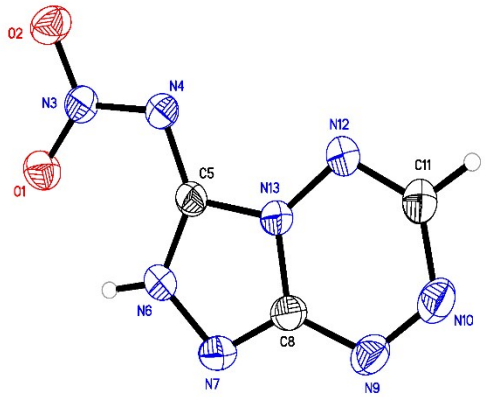


Figure S1. Single-crystal X-ray structure of **3** with numbering.

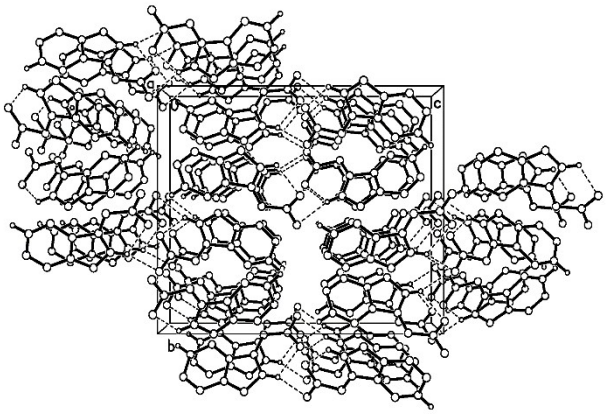


Figure S2. Unit cell view for **3** along a axis, hydrogen bonds are marked as dotted lines.

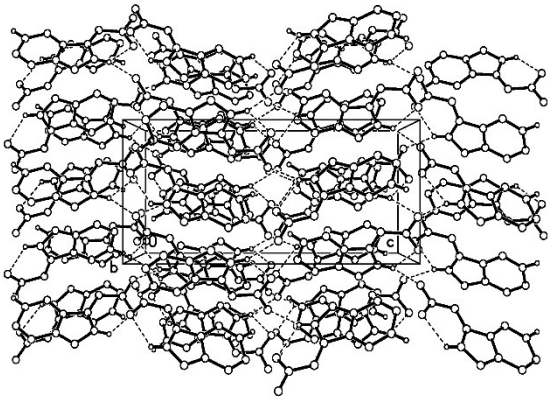


Figure S3. Unit cell view for **3** along b axis, hydrogen bonds are marked as dotted lines.

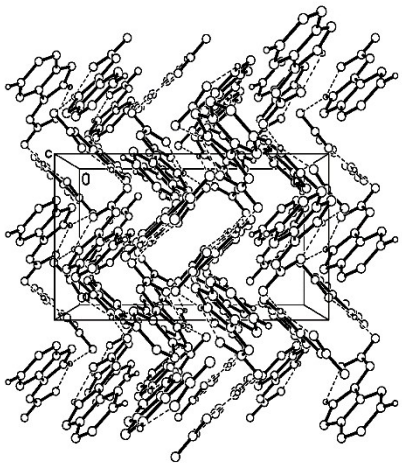


Figure S4. Unit cell view for **3** along c axis, hydrogen bonds are marked as dotted lines.

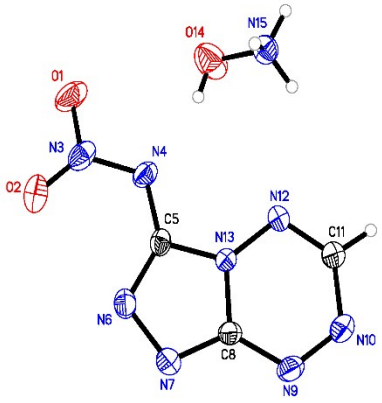


Figure S5. Single-crystal X-ray structure of **5** with numbering.

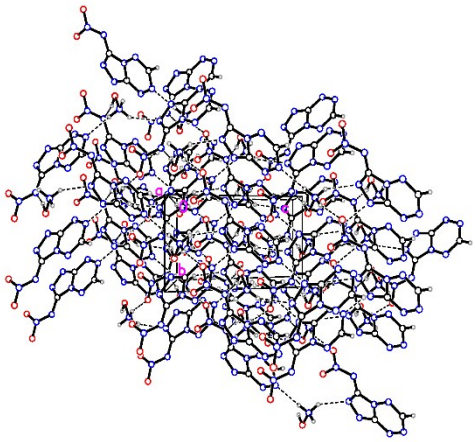


Figure S6. Unit cell view for **5** along a axis, hydrogen bonds are marked as dotted lines.

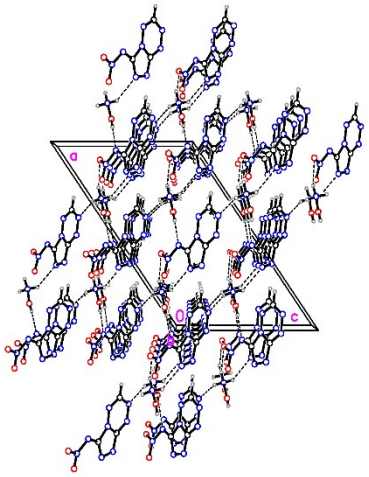


Figure S7. Unit cell view for **5** along b axis, hydrogen bonds are marked as dotted lines.

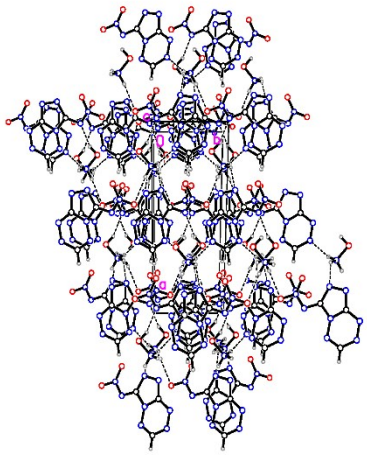


Figure S8. Unit cell view for **5** along c axis, hydrogen bonds are marked as dotted lines.

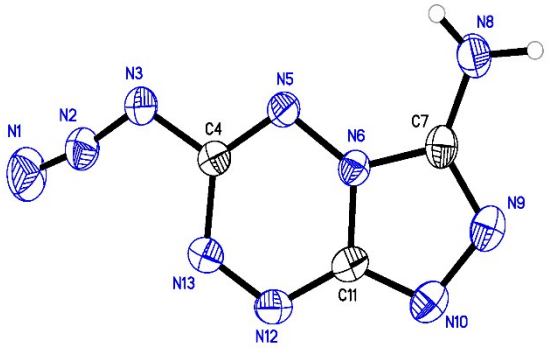


Figure S9. Single-crystal X-ray structures of **13** with numbering.

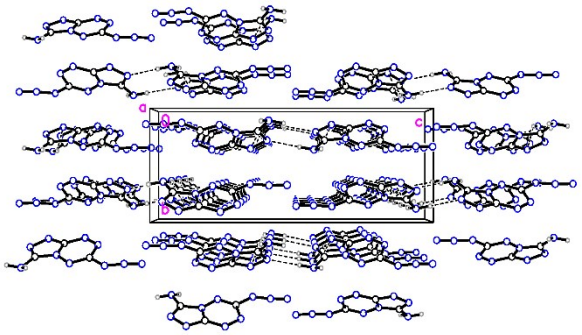


Figure S10. Unit cell view for **13** along a axis, hydrogen bonds as dotted lines.

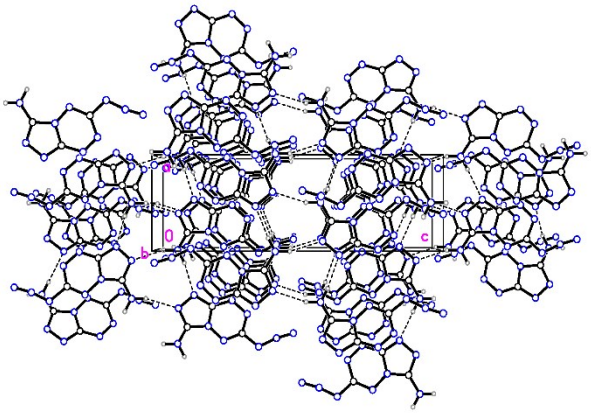


Figure S11. Unit cell view for **13** along c axis, hydrogen bonds are marked as dotted lines.

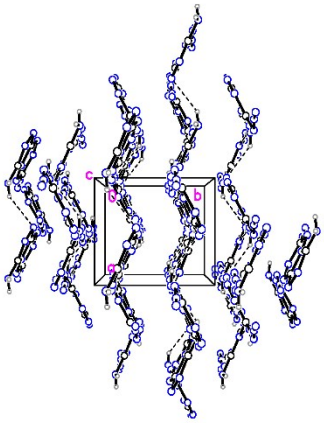


Figure S12. Unit cell view for **13** along c axis, hydrogen bonds are marked as dotted lines.

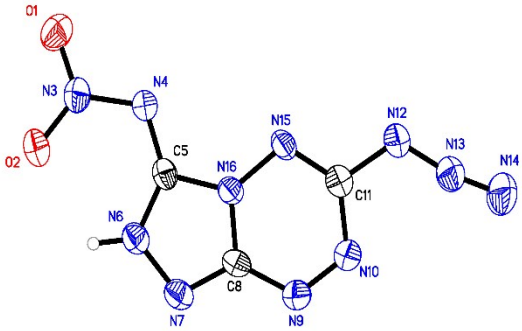


Figure S13. Single-crystal X-ray structures of **14** with numbering

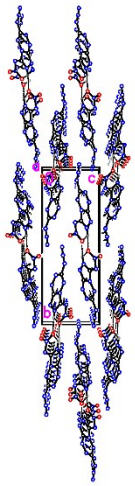


Figure S14. Unit cell view for **14** along a axis, hydrogen bonds are marked as dotted lines.

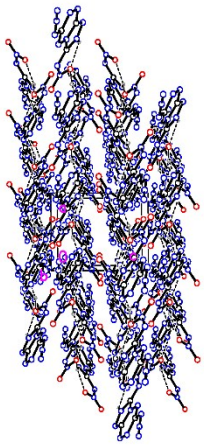


Figure S15. Unit cell view for **14** along b axis, hydrogen bonds are marked as dotted lines.

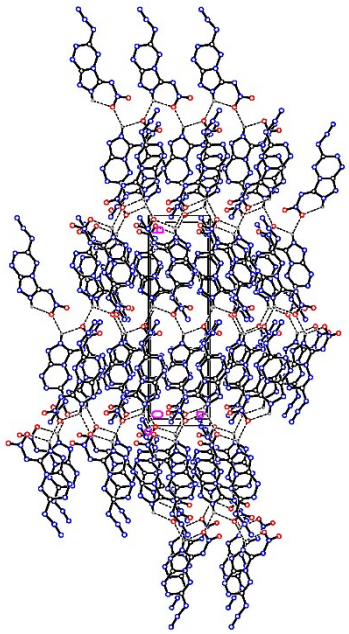


Figure S16. Unit cell view for **14** along b axis, hydrogen bonds are marked as dotted lines.

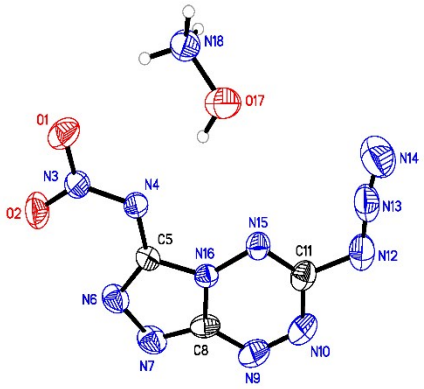


Figure S17. Single-crystal X-ray structures of **17** with numbering.

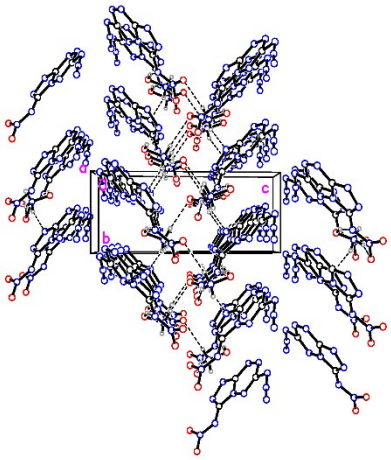


Figure S18. Unit cell view for **17** along a axis, hydrogen bonds are marked as dotted lines.

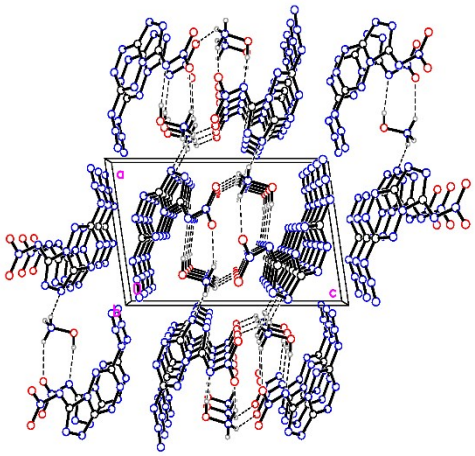


Figure S19. Unit cell view for **17** along b axis, hydrogen bonds are marked as dotted lines.

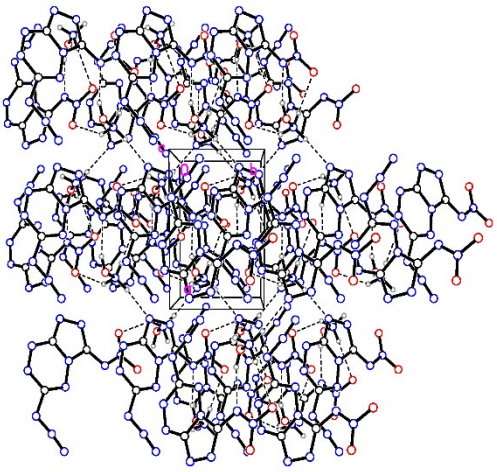


Figure S20. Unit cell view for **17** along c axis, hydrogen bonds are marked as dotted lines.

Table S3. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(19)-H(19)...O(2)	0.86	2.02	2.812(2)	153.6
N(19)-H(19)...O(14)	0.86	2.11	2.571(2)	113.3
N(6)-H(6)...O(1)	0.86	2.10	2.572(2)	114.1
N(6)-H(6)...O(15)#1	0.86	2.08	2.888(2)	155.8

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

Table S4. Hydrogen bonds for **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(14)-H(14)...N(4)	0.841(14)	1.88(2)	2.685(3)	159(5)
N(15)-H(15A)...N(10)#2	0.89	2.09	2.939(3)	159.6
N(15)-H(15B)...O(1)#3	0.89	2.13	2.988(3)	161.9
N(15)-H(15C)...N(6)#1	0.89	2.19	2.890(3)	135.3

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Hydrogen bonds for **13** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8A)...N(9)#1	0.90(3)	2.13(3)	3.0041(19)	164(2)
N8)-H(8B)...N(10)#2	0.87(3)	2.44(3)	3.190(2)	145(2)

Symmetry transformations used to generate equivalent atoms:

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

Table 6. Hydrogen bonds for **14** Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(2)	0.86	2.10	2.574(4)	113.7
N(6)-H(6)...O(18)	0.86	2.04	2.789(4)	144.6
N(22)-H(22)...O(2)#1	0.86	2.06	2.799(4)	143.2
N(22)-H(22)...O(18)	0.86	2.10	2.568(4)	113.4

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

Table 7. Hydrogen bonds for **17** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(14)-H(14)...N(4)	0.841(14)	1.88(2)	2.685(3)	159(5)
N(15)-H(15A)...N(10)#2	0.89	2.09	2.939(3)	159.6
N(15)-H(15B)...O(1)#3	0.89	2.13	2.988(3)	161.9
N(15)-H(15C)...N(6)#1	0.89	2.19	2.890(3)	135.3

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

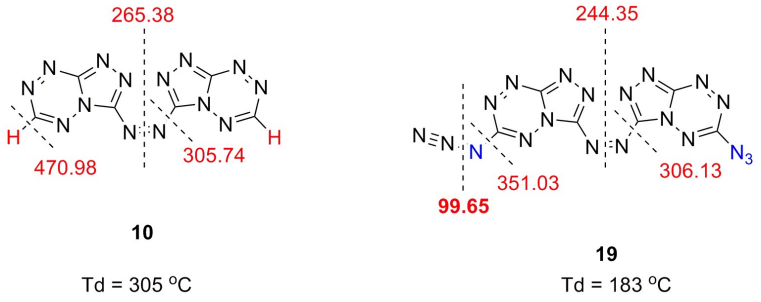


Figure. S21 Bond dissociation energy (BDE) of **10** and **19**[1]

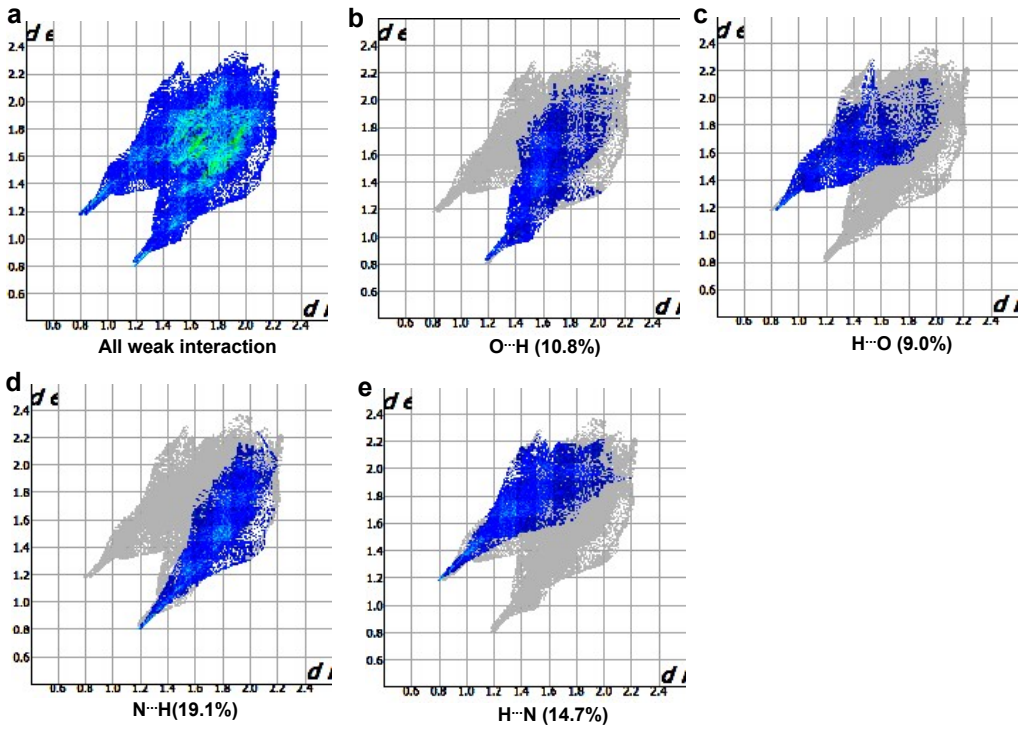


Figure. S22. 2D fingerprint plots for **5**

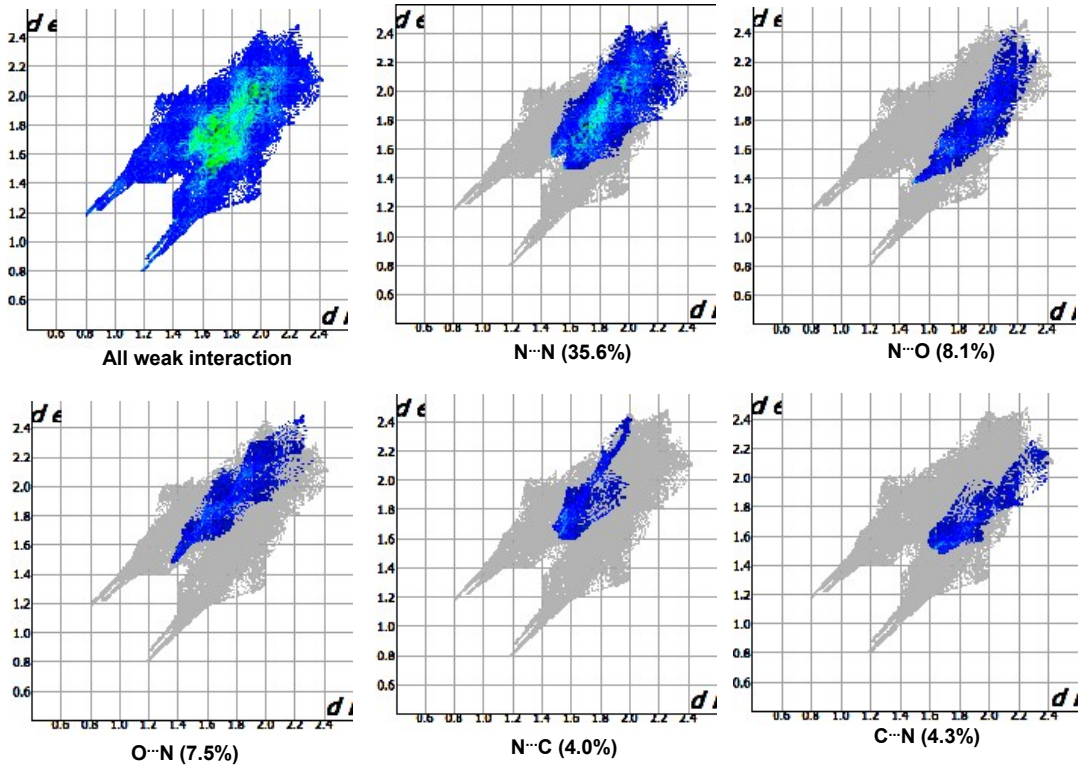


Figure S23. 2D fingerprint plots for **17**

Reference

1 V. D. Ghule, R. Sarangapani, P. M. Jadhav, and S. P. Tewari, *Chem. Papers*, **2011**, 65(3), 380-388.