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Supporting Information

2,4,5-Trinitroimidazole-Based Energetic Salts

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Crystal Structure of 2

Crystals of compound **2** were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 296(2) K using a Bruker/Siemens SMART APEX instrument (Mo Ka radiation, ? = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. At lower temperatures (T < 0ºC) the sample disintegrated. Data were measured using omega scans of 0.3 ° per frame for 20 seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[4] software and refined using SAINTPlus[5] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[6] The structure was solved by direct methods and refined by least squares method on F[5] using the SHELXTL program package.[7] The structure was solved in the space group Pbca (# 61) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection (Figure S1)

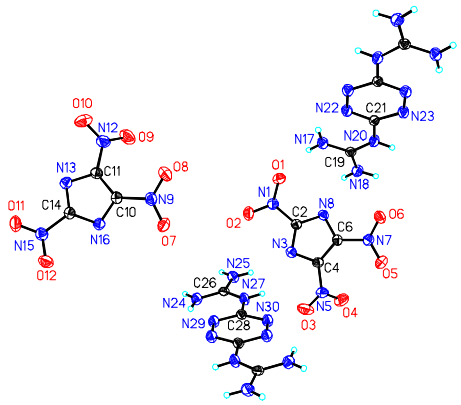

Figure S1. (a)Thermal ellipsoid (30%) plot of **2**. Only symmetry unique non-hydrogen atoms are labeled. Hydrogen atoms are indicated but are unlabeled.

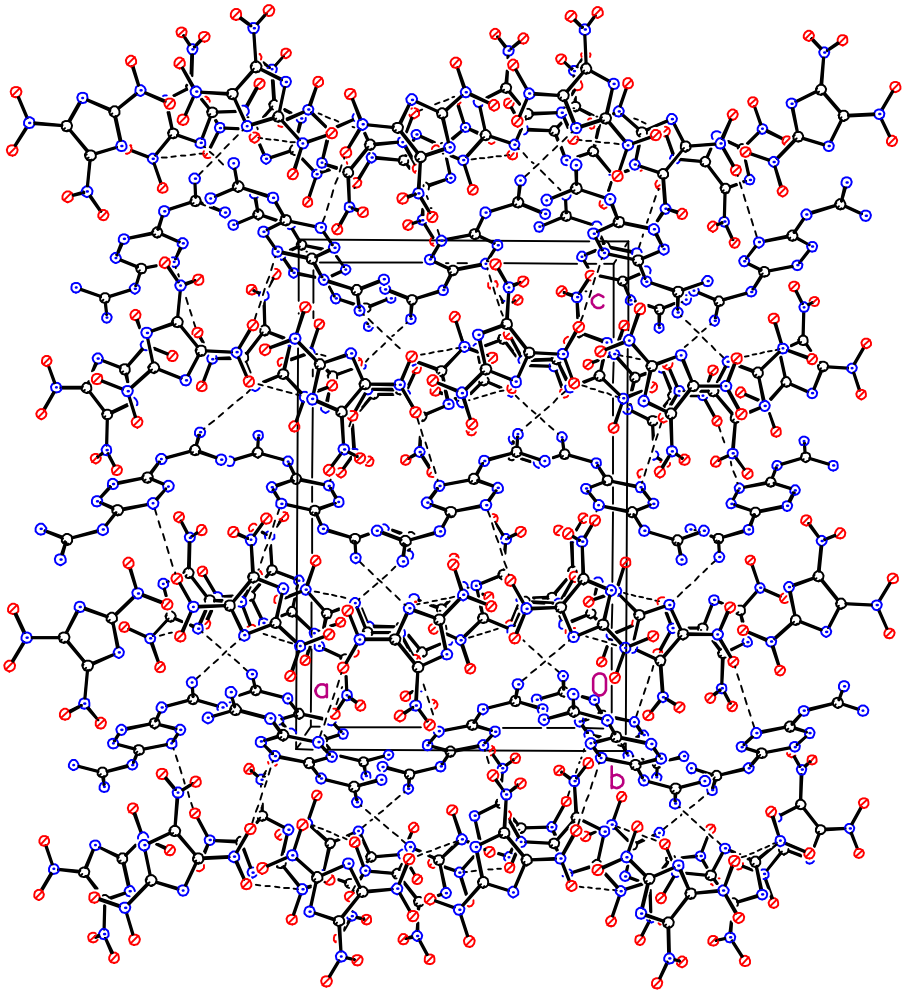

Figure S2. Ball and stick packing plot of **2** viewed down the b axis illustrating the undulating wave-like layers. Hydrogen atoms omitted for clarity. Dashed lines indicate hydrogen bonding.

Crystals of compound **9** were removed from the flask, a suitable crystal was selected, attached to a MiTeGen fiber and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Ka radiation, ? = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of

2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[4] software and refined using SAINTPlus[5] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[6] The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[7] The structure was solved in the space group P2(1) (# 4) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The absolute structure could not be determined. No decomposition was observed during data collection (Figure S2).

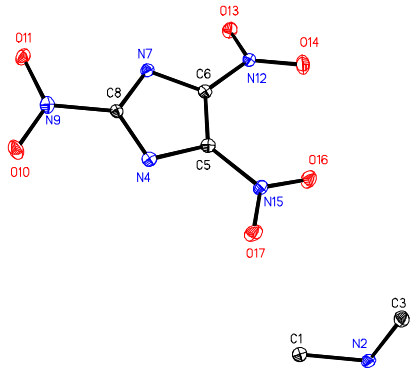

Figure S3. Thermal ellipsoid (30%) plot of **9**. Only symmetry unique non-hydrogen atoms are labelled. Hydrogen atoms are indicated but are unlabeled.

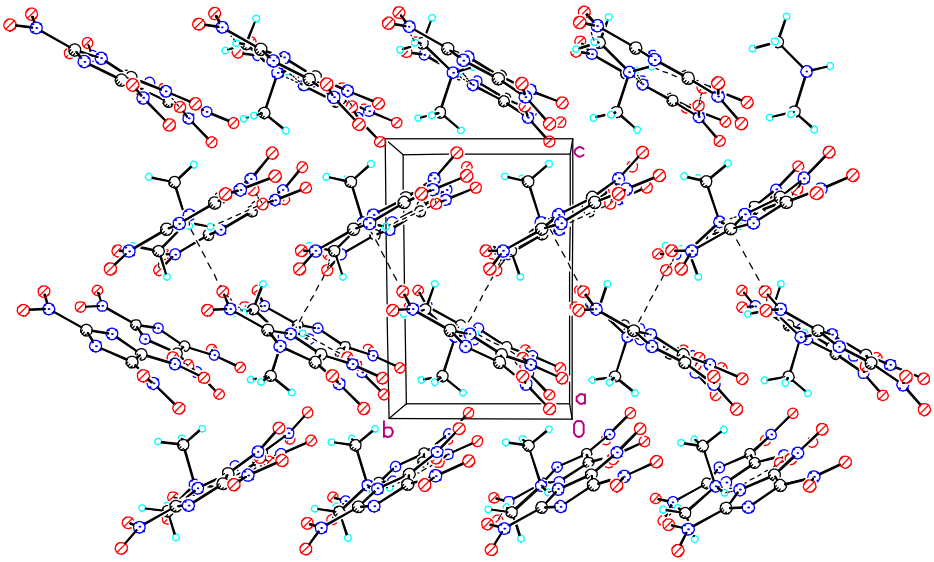

Figure S4. Extended ball and stick packing diagram of 9 showing the sawtooth hydrogen bonded network of hydrogen bonded chains. Dashed lines indicate hydrogen bonding.

2. *Ab Initio* computational data

TABLE S5. Calculated(B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E_0), Zero-Point Energy (ZPE), Values of Thermal Correction (H_T), and Heats of Formation (HOF) of the Compounds or Ions.[a]

Name	E_0	ZPE	H_T	HOF
trinitroimidazole anion	-837.7163568	0.064991	0.012028	-148.5
3,6-diguanidinium tetrazine cation	-703.9503623	0.205184	0.01367	1903.6
3,6-dihydrazine tetrazine cation	-517.2319247	0.147117	0.010586	2302.0
guanidine cation	-205.331961	0.094333	0.006227	566.7
4 amino triazole cation	-297.3150795	0.089607	0.005933	936.3
5 amino 4 H triazole cation	-297.3661712	0.089236	0.006303	804.5
triazole cation	-242.10415	0.07324	0.00457	835.0[8]
imidazole anion	-225.1708943	0.0574	0.004493	57.7
CH_4	-40.39849	0.044791	0.003812	-74.6[9]
CH_3NO_2	-244.5543604	0.049857	0.005272	-74.3[9]
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0[9]
NH_2NH_2	-111.63188	0.053399	0.004202	95.4[9]
$NH_2NH_3^+$	-111.97353	0.06803	0.004309	770.0[8]
NH_3	-56.43462	0.034377	0.003818	-45.9[9]

Table S6. G2 Enthalpy of compounds or ions

	G2 Enthalpy(Hartree)	HOF(kJ/mol)
NH_3	-56.454832	-45.9[9]
NH_4^+	-56.777598	626.4

Guanidine	-205.035186	26.0
Guanidine cation	-205.408542	566.7
Dimethylamino	-134.877374	-18.8[9]
Dimethylamino cation	-135.229903	579.5
Imidazole	-225.826518	132.9[9]
Imidazole anion	-225.272371	57.7
Tetrazine	-295.869844	482.3

Geometry Coordinates

B3LYP/6-31+G(d,p) optimized geometries (Å)

Diguanidine tetrazine cation

C	1.21891000	-0.30838400	-0.00012800
N	0.90492700	0.96876400	-0.00010000
C	-1.21891900	0.30836100	0.00006500
N	0.33730800	-1.28640000	-0.00005200
N	-0.90494300	-0.96876000	0.00003800
N	-0.33729900	1.28639800	-0.00001100
N	-2.54736400	0.72100800	0.00000800
H	-2.64544700	1.71598600	0.00001200
N	2.54736500	-0.72100500	-0.00002400
H	2.64545700	-1.71598200	-0.00007900
C	-3.68683000	-0.01057100	0.00001300
C	3.68683000	0.01057500	0.00002000
N	-3.67402400	-1.31986300	0.00001300
H	-4.52966000	-1.83263200	0.00003100
H	-2.81762800	-1.83159600	0.00001700
N	-4.82544300	0.65346600	0.00002800
H	-5.70026100	0.17445600	-0.00001500
H	-4.86368000	1.64917600	-0.00001600
N	3.67403400	1.31986900	0.00004400
H	2.81764400	1.83161000	-0.00003000
H	4.52967400	1.83262900	0.00008900
N	4.82544100	-0.65346300	0.00003700

H	5.70026100	-0.17445600	0.00012100
H	4.86367600	-1.64917400	0.00020100

Dihydrazine tetrazine cation

C	-1.21836600	0.33054400	0.03144500
C	1.21836600	-0.33053900	-0.03151700
N	0.92846500	0.97676500	-0.06275600
N	-0.33290100	1.33491100	-0.03431300
N	0.33291400	-1.33489400	0.03428800
N	-0.92846400	-0.97675100	0.06272200
N	-2.56196300	0.67823900	0.14535200
H	-2.86253800	1.59699400	-0.17309900
N	2.56197400	-0.67822700	-0.14554000
H	2.86248500	-1.59700400	0.17292100
H	3.89224800	0.39913800	1.02105500
H	4.26658900	0.30896500	-0.61808900
H	-3.89252800	-0.39926000	-1.02073300
H	-2.98435900	-1.26987300	0.09281600
N	3.49853300	0.37776700	0.06593300
N	-3.49854300	-0.37779600	-0.06572600
H	-4.26641500	-0.30896900	0.61850600
H	2.98442900	1.26987600	-0.09267100

Guanidine cation

C	0.00000000	0.00000000	0.00000000
N	-0.92328800	0.94617900	0.00000000
H	-1.89360900	0.72503300	0.00062700
N	-0.35777100	-1.27268000	0.00000000
H	-1.31557200	-1.54295100	-0.00062800
N	1.28105900	0.32650100	0.00000000
H	1.57470200	1.27739700	0.00062600
H	1.99402100	-0.36784300	-0.00062900
H	-0.67845000	1.91079400	-0.00062800
H	0.31890700	-2.00243000	0.00062700

Amino guanidine cation

C	0.50180300	0.01037900	0.00031200

N	0.42059000	1.32116100	-0.00019900
H	-0.49566000	1.72899400	-0.00058500
H	1.22445500	1.91270000	0.00058800
N	1.67295700	-0.61249600	0.00002700
H	1.74196200	-1.60921600	0.00010300
H	2.53406500	-0.10583300	-0.00076200
N	-0.62208200	-0.70669400	0.00020100
H	-0.60800800	-1.70643200	-0.00146800
N	-1.85166700	0.00553400	-0.00003300
H	-2.37328000	-0.16777800	-0.84191600
H	-2.37293500	-0.16724900	0.84219400

Triazole cation

C	1.06781200	-0.42029800	0.00010900
C	-0.67893500	0.90127700	0.00004600
N	-1.03482600	-0.37525900	0.00001900
H	-1.97587900	-0.75959900	0.00001500
H	2.09994900	-0.74013000	0.00012600
H	-1.33110800	1.76370500	0.00006000
N	0.66202000	0.89692400	-0.00007200
H	1.25870500	1.71927200	-0.00014000
N	0.03210100	-1.21725400	-0.00009000

5 amino triazol cation

C	1.46181300	0.57038700	-0.00002200
C	-0.67509100	0.00946600	0.00000300
N	1.46260300	-0.72410300	0.00000500
H	2.34327500	1.19450000	-0.00002900
H	-0.10020500	2.04934300	-0.00031200
H	-0.13059000	-2.04371900	-0.00025400
N	0.12871800	-1.06493700	0.00027400
N	0.16663600	1.07218400	-0.00014000
N	-2.00956000	0.03574400	-0.00017700
H	-2.55012700	-0.81797300	-0.00145800
H	-2.52146500	0.90651800	0.00243300

4 amino triazole cation

C	0.17327200	-1.07585200	-0.00040800
C	0.15861600	1.11430100	-0.00044600
N	-0.64703300	-0.01203200	-0.00018100
H	-0.13714300	-2.11145700	-0.00032200
H	-0.21854600	2.12736000	0.00020900
N	-2.04081200	-0.14197000	0.00039100
H	-2.43008400	0.28136800	0.83991600
H	-2.43052000	0.27985400	-0.83970400
N	1.42022700	0.77809000	0.00008200
N	1.40254600	-0.58318300	0.00030500
H	2.28046500	-1.09415300	0.00085700

G2 optimized geometries (Å)

Imidazole

C	-0.55574700	1.01796500	-0.00000100
C	-1.14844100	-0.22420500	0.00000000
C	0.96069000	-0.58933000	-0.00000200
N	0.79502700	0.76509900	-0.00000600
H	1.53112700	1.45970000	0.00003500
H	-0.95464100	2.02136600	0.00000800
H	-2.20503500	-0.45450900	-0.00002100
H	1.93667600	-1.05576300	-0.00002100
N	-0.20176100	-1.22186700	0.00000800

Imidazole anion

C	-0.89974100	-0.69539900	0.00000600
C	-0.89974100	0.69539900	0.00000100
C	1.09793900	0.00000000	-0.00000100
N	0.39357400	-1.15737100	-0.00001000
H	-1.74451900	-1.38191500	0.00000000
H	-1.74451900	1.38191600	0.00005700
H	2.18825000	0.00000000	0.00009900
N	0.39357500	1.15737100	-0.00001800

Guanidine

C	0.01762200	0.12356900	-0.00018000
N	1.00281500	-0.86773300	0.08409900
H	0.81418400	-1.66607800	-0.51364400
H	1.94418400	-0.51809800	-0.05399300
N	-1.25960800	-0.43321500	-0.08986100
H	-1.41141100	-1.18838500	0.57135700
H	-1.96285800	0.29226900	0.00709100
N	0.16474800	1.39937900	0.01074900
H	1.15448600	1.64986300	-0.04464600

Guanidine cation

C	0.00000000	0.00000100	0.00000000
N	-0.32933100	-1.29225100	0.00000000
H	0.34959600	-2.00922500	-0.22246400
N	1.28378800	0.36091600	0.00000000
H	2.01719100	-0.30023000	0.22246300
N	-0.95445700	0.93133400	-0.00000100
H	-1.91483800	0.70185000	-0.22246000
H	-0.74859400	1.89705400	0.22246400
H	-1.26860100	-1.59682500	0.22246500
H	1.56524200	1.30737200	-0.22246200

Dimethyl amine cation

H	0.00000000	1.16370400	-0.81946600
H	0.00000000	1.16370300	0.81946600
C	-1.25830300	-0.27692000	0.00000000
H	-1.26054700	-0.89799600	0.89398800
H	-2.11558500	0.39454700	-0.00004800
H	-1.26050200	-0.89806700	-0.89393900
C	1.25830300	-0.27692000	0.00000000
H	1.26053300	-0.89801800	-0.89397300
H	2.11558500	0.39454700	0.00001800
H	1.26051600	-0.89804500	0.89395500
N	0.00000000	0.54266700	0.00000000

Dimethyl amine

N	-0.00053452	0.00085577	-0.04941759

H	-0.03406195	0.05919920	0.96648235
C	1.39260121	-0.00230058	-0.47341243
H	1.43025486	0.04110196	-1.56554536
H	1.89431733	0.88661499	-0.08398604
H	1.95850896	-0.89351338	-0.15307776
C	-0.69418000	-1.20744188	-0.47307019
H	-1.71476818	-1.19767521	-0.08339436
H	-0.75086027	-1.21851860	-1.56518766
H	-0.20501525	-2.14297460	-0.15272269

Azide acid

N	0.000000	0.107370	0.000000
N	-0.317697	1.221285	0.000000
N	0.153525	-1.133042	0.000000
H	1.149209	-1.369290	0.000000

Azide anion

N	0.140456	0.000000	0.080766
N	-0.058339	0.000000	1.282372
N	0.339252	0.000000	-1.120840

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