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Supplementary Information

for

Energetic mono-, di-basic 5-dinitromethyltetrazolate: synthesis, properties, and particle processing

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Part A: Crystallographic Data and Structure Refinement Parameters of compound **7** and co-crystallized compound **10**

Table S1. Crystallographic Data and Structure Refinement Parameters.

	Co-crystallized compound 10	**Compound 7**
formula	$C_8H_{16}N_{18}O_5$	$C_{10}H_{14}N_{10}O_4$
mol wt	444.39	338.31
Crystal system	Monoclinic, Cc	Monoclinic, C2/c
a (Å)	11.9753(8)	15.7214(10)
b (Å)	23.2559(16)	12.7935(8)
c (Å)	6.8413(5)	8.1458(5)
α (°)	90	72.11(3)
β(°)	110.384(1)	121.096(1)
γ (°)	90	70.28(2)
V (Å^3)	1786.0(2)	1402.95(15)
Z	4	4
T(K)	90(2)	90(2)
(Å)	0.71073	0.71073
calcd (Mg/m^3)	1.653	1.602
(mm^{-1})	0.138	0.128
F(000)	920	704

crystal size (mm^3)	0.44 x 0.13 x 0.03	0.36 x 0.07 x 0.06
□range (°)	1.75 to 29.00	2.20 to 25.25
Index ranges	-16≤h≤16, -31≤k≤31, -9≤l≤9	-18≤h≤18, -15≤k≤15, -9≤l≤9
no. refl. collected	12564	10924
no. indep. reflections	2372 [R(int) = 0.0305]	1276 [R(int) = 0.0352]
data/restraints/param.	2372 / 2 / 280	1276 / 0 / 111
GOF	1.035	1.019
*R_1 [I>2σ (I)]	0.0336	0.0337
*wR_2 [I>2σ (I)]	0.0752	0.0819
Largest diff. peak, hole (eÅ^{-3})	0.288, -0.196	0.223, -0.198

- $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma [w(F_o^2)^2]\}^{1/2}$

Table S2. Hydrogen bonds for Co-crystallized compound 10 [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(5)	0.90	2.19	3.036(3)	156.1
N(1)-H(1B)...N(5)#1	0.89	2.33	3.142(3)	151.4
N(4)-H(4)...N(18)#2	0.88	1.83	2.653(3)	153.8
N(4)-H(4)...O(4)#3	0.88	2.51	2.964(2)	113.1
N(14)-H(14)...N(25)#2	0.88	1.92	2.741(3)	154.7
N(15)-H(15A)...O(5)#4	0.89	2.09	2.951(3)	163.7
N(15)-H(15B)...N(24)#4	0.89	2.21	3.042(3)	154.2
N(21)-H(21A)...N(15)#1	0.89	2.51	3.127(3)	126.2
N(21)-H(21A)...O(1)#4	0.89	2.52	3.274(3)	141.9
N(21)-H(21B)...O(2)#3	0.90	2.28	3.160(3)	166.3
N(21)-H(21B)...O(1)#3	0.90	2.54	3.258(3)	137.9
O(5)-H(5A)...N(11)#2	0.85	2.11	2.940(3)	165.5
O(5)-H(5A)...O(1)#2	0.85	2.41	2.943(2)	121.4
O(5)-H(5B)...N(19)#5	0.85	2.01	2.851(3)	171.7
C(3)-H(3)...O(2)#3	0.95	2.38	3.331(3)	176.5
C(3)-H(3)...O(4)#3	0.95	2.34	2.886(3)	116.4

Symmetry transformations used to generate equivalent atoms:

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

#3 x+1/2,y-1/2,z #4 x+1/2,-y+1/2,z-1/2 #5 x,y,z+1

Table S3. Hydrogen bonds for Co-crystallized compound 7 [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...N(8)#2	0.88	1.97	2.7566(18)	148.3
N(4)-H(4)...O(13)#3	0.88	2.47	2.9730(17)	116.6
C(1)-H(1A)...O(12)#4	0.98	2.50	3.309(2)	139.4
C(3)-H(3)...O(13)#3	0.95	2.48	2.9869(19)	113.1
C(3)-H(3)...O(12)#4	0.95	2.37	3.1615(19)	140.5
C(6)-H(6)...O(12)#5	0.95	2.47	3.2706(19)	142.0

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+1/2,-y+1/2,-z+2 #5 x,-y,z+1/2

Part B: *Ab Initio* computational data

TABLE S4. 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
5-dinitromethyltetrazole anion	-704.7683531	0.067177	0.010238	70.0
5-dinitromethyltetrazole dianion	-704.1153037	0.0513873	0.0127237	228.7105114
amino guanidine	-260.5457263	0.114876	0.006214	667.4
guanidine cation	-205.331961	0.094333	0.006227	566.7
Tetrazole anion	-257.21883	0.03382	0.00422	170.0
tetrazole	-257.7488254	0.046853	0.00443	334.5
urea	-224.8323997	0.063642	0.005402	-245.8[9]
1-methylimidazolium	-265.3210147	0.112924	0.006392	680.6
4 amino triazole cation	-297.3150795	0.089607	0.005933	936.3
3 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 cation	-226.10404	0.08524	0.00473	711.5
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 S5. 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
Carbohydride cation	-335.720388	663.4
Carbohydride	-335.387052	8.5
urea	-224.933512	-245.8[9]
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)

5-dinitromethyltetrazole anion

C	-0.87079200	-0.10193200	0.00408600
N	-1.72930100	0.94338400	-0.07646800
N	-2.99925200	0.49547300	0.02634300
N	-2.90697400	-0.79224400	0.15357800
N	-1.61851000	-1.20692000	0.14766000
C	0.56623900	0.01167900	-0.01012000
N	1.36387800	-1.17994100	-0.00273700
O	0.95046500	-2.14330400	-0.66895800
O	2.40019200	-1.21508200	0.67520600
N	1.20434800	1.24215000	-0.04321300
O	0.46933300	2.28651200	-0.00411300
O	2.44003100	1.33579300	-0.16215400
H	-1.45218600	1.91684100	-0.11977800

5-dinitromethyltetrazole dianion

C	-0.90742600	-0.00005400	-0.00000200
N	-1.66304400	0.09521800	-1.11040200
C	0.56780000	-0.00000400	-0.00001200
N	1.25141900	-1.21847000	-0.00675400
O	0.54851500	-2.26475300	-0.11492800

O	2.50252800	-1.30284100	0.10885400
N	1.25133200	1.21851200	0.00677200
O	0.54839700	2.26473900	0.11483800
O	2.50247600	1.30293100	-0.10881600
N	-2.92962800	0.05697800	-0.66273000
N	-2.92960200	-0.05699700	0.66277200
N	-1.66298600	-0.09527800	1.11041500

aminoguanidine 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

Tetrazole

C	-0.96258400	-0.52379200	0.00001800
N	-0.69368800	0.79729100	0.00002200
H	-1.30811800	1.59924600	0.00003000
H	-1.95172700	-0.95502400	0.00001800
N	0.64923400	0.96367000	-0.00006800
N	0.17991700	-1.17893300	-0.00006000
N	1.15530100	-0.22509500	0.00008300

Urea

C	0.0708549875,	0.1346947463,	0.0909678525
N	0.4639946892,	0.026372018,	1.4157932148
H	0.095704513,	-0.7902697546,	1.8824224155
H	0.5072127185,	0.8620689899,	1.9819400834
N	0.3437976012,	1.3639658806,	-0.4893499693
H	0.231291075,	1.3712789641,	-1.4932136095
H	1.1231165879,	1.9046519482,	-0.1412461807
O	-0.4726193123,	-0.7791715185,	-0.5163516094

3-amino triazole 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

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

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

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

NH2NHCONHNH2 (carbohydrazide)

C	0.04385200	0.55239500	-0.00446600
O	0.51725600	1.67626400	0.08169500
N	-1.33544400	0.37820200	-0.21359500
H	-1.84487000	1.20153000	0.09968900

N	0.72425900	-0.63719100	0.06031600
H	0.19711000	-1.47089200	-0.17882300
N	-1.90160500	-0.88752000	0.06584200
H	-2.27707700	-0.91841900	1.01435100
H	-2.66762200	-1.03892600	-0.58554800
N	2.12277800	-0.61308500	-0.01825100
H	2.49598800	-1.23364200	0.69463100
H	2.42539600	-0.94697900	-0.93124300

NH2NHCONHNH2 cation

`C	-0.84420000	0.01729900	-0.00384100
O	-2.05335200	-0.05809200	0.02748500
N	-0.07051800	-1.12207300	-0.39284000
H	-0.63852900	-1.96717700	-0.31693800
N	-0.11981100	1.15164800	0.30552200
H	-0.71064300	1.98073500	0.37088700
N	1.18776300	1.31143400	-0.22808000
H	1.15357100	1.70171200	-1.17417800
H	1.68844000	1.97001900	0.37005400
H	1.16390600	-1.49425300	1.24733000
H	1.74276400	-1.99977300	-0.25087300
H	1.65650800	-0.31186500	0.07976900
N	1.20770800	-1.27221800	0.24070100

Part C : Properties of energetic 5-dinitromethyltetrazolates

Salt	D^a	Tm^b	Td^c	OB^d	ΔH_f^e *cation*	ΔH_f^e *anion*	*Lattice energy*^{f}	ΔH_f^g	P^h	vD^i	$I_{sp}{}^j$
2	1.66	-	161.1	-45	667.4	70.0	482.0	255.4	26.3	8253	230.7
3	1.61	-	152.6	-54	667.4	228.7	1260.5	303.1	24.4	8312	212.9
4	1.87	-	178.9	-36	663.4	70.0	489.2	244.2	37.7	9188	246.3
5	1.62	-	165.8	-40	663.4	228.7	1218.9	336.7	26.2	8319	237.7
6	1.67	-	104.5	-75	680.5	70.0	478.9	271.7	21.2	7436	209.0
7	1.60	-	115.7	-108	680.5	228.7	1234.6	355.3	19.7	6959	191.9
8	1.84	-	127.8	-43	835.0	70.0	497.7	407.3	31.7	8580	233.3
9	1.86	-	84.5	-44	806.3	70.0	491.4	384.9	33.1	8787	226.9
10	1.76	149.5	193.4	-44	936.3	70.0	484.4	521.9	29.4	8414	240.9
TNT	1.65	-	300.0	-74				-70.5	19.5	6881	
NTO	1.92	-		-25				-237.8	31.1	8558	
TNAZ	1.84	-	240.0	-17				45.3	36.4	9006	
ADN	1.81	92	127.0	25.8	626.4	-156.2	592.9	-149.7	23.7	8074	

[a] density (g/cm^3); [b] melting point *(°C)*; [c] decomposition temperature *(°C)*; [d] oxygen balance (OB) - index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) =1600[(d - 2a - b/2)/M_W]; [e] Heat of formation cation and anion (kJ/mol); [f] Lattice energy of salt (kJ/mol); [g] Heat of formation of salt (kJ/mol); [h] detonation pressure (GPa); [i] detonation velocity (m s^{-1}); [j] I_{sp} - specific impulse (s).