4-Amino-3,5-Dinitropyrazolate Salts – Highly Insensitive Energetic Materials

Yanqiang Zhang,[a] Yangen Huang,[b] Damon A. Parrish,[c] and Jean'ne M. Shreeve*,[a]

[a] Dr. Y. Zhang, and Prof. Dr. J. M. Shreeve

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

Fax: (+1) 208-885-9146

E-mail: jshreeve@uidaho.edu

[b] Dr. Y. Huang

College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

[c] Dr. D. A. Parrish

Naval Research Laboratory, Code 6030, Washington, D.C. 20375-5001, USA

Part A: Crystallographic Data and Structure Refinement Parameters of Compounds **9** and **15**.

S-1 - Table 1s. Bond lengths and angles for **9**.

S-2 - Table 2s. Hydrogen bond data for **9**.

S-3 - Table 3s. Bond lengths and angles for **15.**

S-4 - Talbe 4s. Hydrogen bond data for **15.**

Part B: Ab Initio Computational Data

S-5 - Scheme 1s Isodesmic reactions for the nitrogen-rich cations and 4-amino-3,5-dinitro-pyrazolate anions.

S-6 - Table 5s. Calcualted (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 nitrogen-rich cations and 4-amino-3,5-dinitropyrazolate anion.

S-1 - Table 1s. Bond lengths and angles for **9**.

N(1)-N(2)	1.3208(16)	N(1)-C(5)	1.3678(17)
N(2)-C(3)	1.3682(17)	C(3)-N(6)	1.3985(17)
C(3)-C(4)	1.4095(19)	C(4)-N(9)	1.3399(17)
C(4)-C(5)	1.4057(18)	C(5)-N(10)	1.3966(17)
N(6)-O(7)	1.2345(15)	N(6)-O(8)	1.2586(15)
N(9)-H(9A)	0.8800	N(9)-H(9B)	0.8800
N(10)-O(12)	1.2435(16)	N(10)-O(11)	1.2515(15)
O(13)-C(14)	1.221(2)	C(14)-N(15)	1.3613(16)
C(14)-N(15)#1	1.3613(16)	N(15)-N(16)	1.4122(16)
N(15)-H(15)	0.8800	N(16)-H(16A)	0.9100
N(16)-H(16B)	0.9100	N(16)-H(16C)	0.9100
N(2)-N(1)-C(5)	107.84(11)	N(1)-N(2)-C(3)	107.49(11)
N(2)-C(3)-N(6)	121.67(12)	N(2)-C(3)-C(4)	112.54(12)
N(6)-C(3)-C(4)	125.79(12)	N(9)-C(4)-C(5)	130.56(13)
N(9)-C(4)-C(3)	129.77(13)	C(5)-C(4)-C(3)	99.65(11)
N(1)-C(5)-N(10)	120.24(12)	N(1)-C(5)-C(4)	112.48(12)
N(10)-C(5)-C(4)	127.27(12)	O(7)-N(6)-O(8)	122.57(11)
O(7)-N(6)-C(3)	121.21(11)	O(8)-N(6)-C(3)	116.22(11)
C(4)-N(9)-H(9A)	120.0	C(4)-N(9)-H(9B)	120.0
H(9A)-N(9)-H(9B)	120.0	O(12)-N(10)-O(11)	122.39(11)
O(12)-N(10)-C(5)	119.27(11)	O(11)-N(10)-C(5)	118.34(11)
O(13)-C(14)-N(15)	124.92(8)	O(13)-C(14)-N(15)#1	124.92(8)
N(15)-C(14)-N(15)#1	110.16(17)	C(14)-N(15)-N(16)	119.10(12)
C(14)-N(15)-H(15)	120.4	N(16)-N(15)-H(15)	120.4
N(15)-N(16)-H(16A)	109.5	N(15)-N(16)-H(16B)	109.5
H(16A)-N(16)-H(16B)	109.5	N(15)-N(16)-H(16C)	109.5
H(16A)-N(16)-H(16C)	109.5	H(16B)-N(16)-H(16C)	109.5

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

S-2 - Table 2s. Hydrogen bond data for **9**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(9)-H(9A)...O(11)	0.88	2.36	2.8896(16)	119.1
N(9)-H(9B)...O(8)	0.88	2.22	2.7747(16)	120.3
N(9)-H(9B)...O(8)	0.88	2.22	2.7747(16)	120.3
N(15)-H(15)...O(8)#2	0.88	2.25	2.9203(16)	133.3
N(16)-H(16A)...O(7)	0.91	2.27	2.8911(16)	124.7
N(16)-H(16B)...N(1)#3	0.91	2.02	2.8902(16)	159.0
N(16)-H(16C)...N(2)	0.91	2.04	2.8748(17)	152.4

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

S-3 - Table 3s. Bond lengths and angles for **15.**

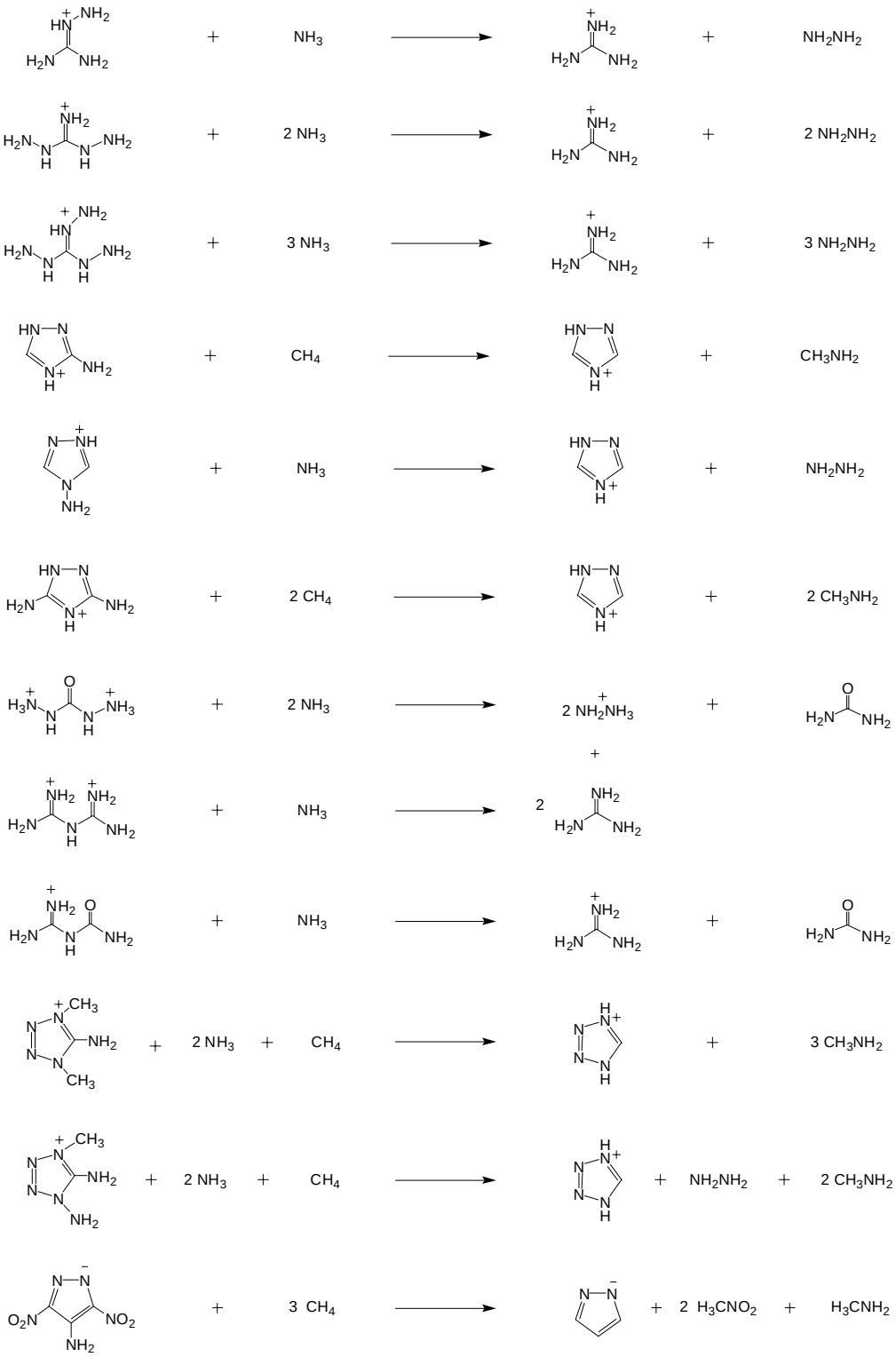
N(1A)-C(5A)	1.3452(19)	N(1A)-N(2A)	1.3708(17)
N(1A)-N(6A)	1.3921(17)	N(2A)-N(3A)	1.2714(18)
N(3A)-N(4A)	1.3738(17)	N(4A)-C(5A)	1.3334(18)
N(4A)-C(7A)	1.4578(19)	C(5A)-N(8A)	1.3130(19)
N(6A)-H(6AA)	0.919(18)	N(6A)-H(6AB)	0.858(19)
C(7A)-H(7AA)	0.9800	C(7A)-H(7AB)	0.9800
C(7A)-H(7AC)	0.9800	N(8A)-H(8AA)	0.8800
N(8A)-H(8AB)	0.8800	N(9A)-N(10A)	1.3225(16)
N(9A)-C(13A)	1.3672(18)	N(10A)-C(11A)	1.3680(17)
C(11A)-N(14A)	1.3971(17)	C(11A)-C(12A)	1.4045(19)
C(12A)-N(17A)	1.3387(18)	C(12A)-C(13A)	1.4094(18)
C(13A)-N(18A)	1.3952(17)	N(14A)-O(15A)	1.2413(15)
N(14A)-O(16A)	1.2528(15)	N(17A)-H(17A)	0.8800
N(17A)-H(17B)	0.8800	N(18A)-O(20A)	1.2453(15)
N(18A)-O(19A)	1.2507(15)	N(1B)-C(5B)	1.3425(18)
N(1B)-N(2B)	1.3664(16)	N(1B)-N(6B)	1.3809(17)
N(2B)-N(3B)	1.2768(17)	N(3B)-N(4B)	1.3737(17)
N(4B)-C(5B)	1.3371(19)	N(4B)-C(7B)	1.4572(18)
C(5B)-N(8B)	1.3098(19)	N(6B)-H(6BA)	0.887(18)
N(6B)-H(6BB)	0.85(2)	C(7B)-H(7BA)	0.9800
C(7B)-H(7BB)	0.9800	C(7B)-H(7BC)	0.9800
N(8B)-H(8BA)	0.8800	N(8B)-H(8BB)	0.8800
N(9B)-N(10B)	1.3210(16)	N(9B)-C(13B)	1.3662(17)
N(10B)-C(11B)	1.3664(17)	C(11B)-N(14B)	1.3970(18)
C(11B)-C(12B)	1.4062(19)	C(12B)-N(17B)	1.3430(17)
C(12B)-C(13B)	1.4022(19)	C(13B)-N(18B)	1.3977(18)
N(14B)-O(15B)	1.2460(16)	N(14B)-O(16B)	1.2488(15)
N(17B)-H(17C)	0.8800	N(17B)-H(17D)	0.8800
N(18B)-O(20B)	1.2396(16)	N(18B)-O(19B)	1.2504(15)
C(5A)-N(1A)-N(2A)	110.03(12)	C(5A)-N(1A)-N(6A)	123.93(12)
N(2A)-N(1A)-N(6A)	124.99(12)	N(3A)-N(2A)-N(1A)	107.52(12)
N(2A)-N(3A)-N(4A)	108.31(11)	C(5A)-N(4A)-N(3A)	109.79(12)
C(5A)-N(4A)-C(7A)	129.02(12)	N(3A)-N(4A)-C(7A)	121.16(12)
N(8A)-C(5A)-N(4A)	128.91(13)	N(8A)-C(5A)-N(1A)	126.76(13)
N(4A)-C(5A)-N(1A)	104.33(12)	N(1A)-N(6A)-H(6AA)	105.1(11)
N(1A)-N(6A)-H(6AB)	108.1(12)	H(6AA)-N(6A)-H(6AB)	114.6(17)
N(4A)-C(7A)-H(7AA)	109.5	N(4A)-C(7A)-H(7AB)	109.5
H(7AA)-C(7A)-H(7AB)	109.5	N(4A)-C(7A)-H(7AC)	109.5
H(7AA)-C(7A)-H(7AC)	109.5	H(7AB)-C(7A)-H(7AC)	109.5
C(5A)-N(8A)-H(8AA)	120.0	C(5A)-N(8A)-H(8AB)	120.0
H(8AA)-N(8A)-H(8AB)	120.0	N(10A)-N(9A)-C(13A)	107.42(11)
N(9A)-N(10A)-C(11A)	108.17(11)	N(10A)-C(11A)-N(14A)	120.84(12)
N(10A)-C(11A)-C(12A)	111.94(11)	N(14A)-C(11A)-C(12A)	127.21(12)
N(17A)-C(12A)-C(11A)	130.28(12)	N(17A)-C(12A)-C(13A)	129.54(13)
C(11A)-C(12A)-C(13A)	100.18(11)	N(9A)-C(13A)-N(18A)	121.55(12)
N(9A)-C(13A)-C(12A)	112.28(11)	N(18A)-C(13A)-C(12A)	126.17(13)
O(15A)-N(14A)-O(16A)	123.10(11)	O(15A)-N(14A)-C(11A)	119.70(12)
O(16A)-N(14A)-C(11A)	117.20(11)	C(12A)-N(17A)-H(17A)	120.0
C(12A)-N(17A)-H(17B)	120.0	H(17A)-N(17A)-H(17B)	120.0

O(20A)-N(18A)-O(19A)	122.13(11)	O(20A)-N(18A)-C(13A)	120.04(12)
O(19A)-N(18A)-C(13A)	117.84(11)	C(5B)-N(1B)-N(2B)	110.49(11)
C(5B)-N(1B)-N(6B)	122.98(12)	N(2B)-N(1B)-N(6B)	126.39(11)
N(3B)-N(2B)-N(1B)	107.53(11)	N(2B)-N(3B)-N(4B)	107.93(11)
C(5B)-N(4B)-N(3B)	110.06(11)	C(5B)-N(4B)-C(7B)	128.66(12)
N(3B)-N(4B)-C(7B)	121.28(12)	N(8B)-C(5B)-N(4B)	129.55(13)
N(8B)-C(5B)-N(1B)	126.46(13)	N(4B)-C(5B)-N(1B)	103.99(12)
N(1B)-N(6B)-H(6BA)	109.4(11)	N(1B)-N(6B)-H(6BB)	109.5(11)
H(6BA)-N(6B)-H(6BB)	112.8(16)	N(4B)-C(7B)-H(7BA)	109.5
N(4B)-C(7B)-H(7BB)	109.5	H(7BA)-C(7B)-H(7BB)	109.5
N(4B)-C(7B)-H(7BC)	109.5	H(7BA)-C(7B)-H(7BC)	109.5
H(7BB)-C(7B)-H(7BC)	109.5	C(5B)-N(8B)-H(8BA)	120.0
C(5B)-N(8B)-H(8BB)	120.0	H(8BA)-N(8B)-H(8BB)	120.0
N(10B)-N(9B)-C(13B)	108.14(11)	N(9B)-N(10B)-C(11B)	107.36(11)
N(10B)-C(11B)-N(14B)	121.12(12)	N(10B)-C(11B)-C(12B)	112.32(12)
N(14B)-C(11B)-C(12B)	126.21(12)	N(17B)-C(12B)-C(13B)	130.03(13)
N(17B)-C(12B)-C(11B)	129.79(13)	C(13B)-C(12B)-C(11B)	100.18(11)
N(9B)-C(13B)-N(18B)	120.66(12)	N(9B)-C(13B)-C(12B)	112.00(12)
N(18B)-C(13B)-C(12B)	127.27(12)	O(15B)-N(14B)-O(16B)	122.34(12)
O(15B)-N(14B)-C(11B)	119.97(12)	O(16B)-N(14B)-C(11B)	117.67(12)
C(12B)-N(17B)-H(17C)	120.0	C(12B)-N(17B)-H(17D)	120.0
H(17C)-N(17B)-H(17D)	120.0	O(20B)-N(18B)-O(19B)	123.28(12)
O(20B)-N(18B)-C(13B)	119.23(11)	O(19B)-N(18B)-C(13B)	117.49(11)

S-4 - Table 4s. Hydrogen bond data for **15.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6A)-H(6AA)...N(10B)#1	0.919(18)	2.232(18)	3.0263(18)	144.3(15)
N(6A)-H(6AB)...O(20A)#2	0.858(19)	2.23(2)	3.0771(17)	167.1(16)
N(8A)-H(8AA)...N(10A)#3	0.88	2.03	2.8756(17)	160.2
N(17A)-H(17A)...O(16A)	0.88	2.32	2.8531(16)	119.4
N(17A)-H(17B)...O(19A)	0.88	2.26	2.8143(16)	120.5
N(6B)-H(6BA)...N(9A)#2	0.887(18)	2.105(19)	2.9882(17)	173.7(16)
N(6B)-H(6BB)...O(19B)	0.85(2)	2.605(19)	3.2992(17)	139.6(14)
N(8B)-H(8BA)...N(9B)#1	0.88	2.00	2.8441(17)	161.2
N(8B)-H(8BB)...O(16A)#1	0.88	2.10	2.9360(16)	159.6
N(17B)-H(17D)...O(16B)	0.88	2.28	2.8221(17)	119.6
N(17B)-H(17C)...O(19B)	0.88	2.31	2.8522(17)	119.6

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



S-5 - Scheme 1s The isodesmic reactions for the nitrogen-rich cations and 4-amino-3,5-dinitro-pyrazolate anions.

S-6 - Table 5s. Calcualted (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 nitrogen-rich cations and 4-amino-3,5-dinitropyrazolate anion.

Name	E_0	ZPE	H_T	HoF
ammonium	-56.755055	0.049632	0.003819	626.4
hydrazinium	-111.97353	0.068030	0.004309	770.0
guanidinium	-205.33196	0.094331	0.006227	566.7
amino-guanidinium	-260.54573	0.114880	0.006214	667.4
diamino-guanidinium	-315.75835	0.133610	0.007123	769.0
triamino-guanidinium	-370.97072	0.152308	0.008131	871.5
triazolium	-242.10415	0.073240	0.004570	835.0
3-amino-triazolium	-297.36617	0.089236	0.006303	804.5
4-amino-triazolium	-297.31508	0.089607	0.005933	936.3
3,5-diamino-triazolium	-352.49256	0.105212	0.008091	764.0
carbohydrazinium	-335.66640	0.125371	0.008293	1764.6
biguanidium	-353.93805	0.141845	0.008852	1618.0
N-carbamoyl-guanidinium	-373.72913	0.115144	0.009159	350.6
1,4-dimethyl-5-mino-tetrazolium	-391.63602	0.131862	0.009638	887.7
1,5-diamino-4-mthyl-tetrazolium	-407.63759	0.121201	0.009041	974.3
CH_4	-40.379622	0.044793	0.003812	-74.6[a]
NH_3	-56.415465	0.034384	0.003819	-45.9[a]
CH_3NH_2	-95.593840	0.064031	0.004380	-23.5[a]
NH_2NH_2	111.583692	0.053312	0.004211	95.4[a]
CH_3NO_2	244.478482	0.049842	0.005298	-81.0[a]
NH_2CONH_2	224.756057	0.063650	0.005401	-235.5[a]
triazolium	-242.00879	0.073241	0.004572	835.0[b]
tetrazolium	-257.98206	0.060292	0.004482	1016.5[b]
pyrazolate	225.049836	0.056611	0.004551	124.2[b]

[a] Data from NIST Chemistry WebBook; [b] Data calculated with the G2 method by using the Gaussian 03 program.