Supporting Information

3-Nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine (HANTT) and its energetic salts: highly thermally stable energetic materials with low sensitivity

Chengming Bian, [a] Man Zhang, [a] Chuan Li [a] and Zhiming Zhou* [a,b]

[a] School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing, 100081, R. P. China

[b] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, R. P. China

E-mail: zzm@bit.edu.cn

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1 X-ray crystallography

Crystals of **2**, **3** and **9** was removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **2** was collected at 153(2) K while for **3** and **9** were collected at 163(2) K, using a Rigaku Saturn724 CCD (AFC10/Saturn724+ for 7) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear -SM Expert 2.0 r2 software.[1] The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL-97 system of programs.[2] Structure were solved in the space group *P*2(1)*/c* for **2**, Pī for **3**, *PC2/c* for **9**, by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. Band angles and dihedral angles of the data collection and refinement are given in Table S1, S2, S3.

Table S1. Band angles and dihedral angles for the structure of **2**.

C1—N1—N2	110.21 (10)	N7—N8—H8	117.5 (11)
C1—N1—C3	128.46 (12)	N9—N8—H8	128.3 (11)
N2—N1—C3	121.27 (11)	C3—N9—N8	99.73 (11)
C2—N2—N1	99.98 (10)	N4—C1—N3	125.92 (12)
C1—N3—C2	101.78 (10)	N4—C1—N1	125.40 (11)
C1—N4—H4A	118.1 (11)	N3—C1—N1	108.67 (11)
C1—N4—H4B	120.7 (13)	N2—C2—N3	119.36 (12)
H4A—N4—H4B	121.2 (17)	N2—C2—N5	120.64 (11)
O2—N5—O1	125.05 (12)	N3—C2—N5	119.97 (11)
O2—N5—C2	118.07 (11)	N9—C3—N6	114.99 (11)
O1—N5—C2	116.88 (11)	N9—C3—N1	123.36 (12)
N7—N6—C3	104.06 (11)	N6—C3—N1	121.65 (12)
N8—N7—N6	107.00 (10)	H3A—O3—H3B	108.5 (19)
N7—N8—N9	114.22 (11)		
C1—N1—N2—C2	0.13 (14)	C1—N3—C2—N5	−177.70 (12)
C3—N1—N2—C2	−177.22 (12)	O2—N5—C2—N2	−0.1 (2)

C3—N6—N7—N8	0.00 (14)	O1—N5—C2—N2	−179.59 (13)
N6—N7—N8—N9	−0.10 (15)	O2—N5—C2—N3	177.92 (13)
N7—N8—N9—C3	0.16 (14)	O1—N5—C2—N3	−1.6 (2)
C2—N3—C1—N4	−179.26 (14)	N8—N9—C3—N6	−0.16 (15)
C2—N3—C1—N1	−0.23 (14)	N8—N9—C3—N1	179.15 (12)
N2—N1—C1—N4	179.10 (14)	N7—N6—C3—N9	0.11 (15)
C3—N1—C1—N4	−3.8 (2)	N7—N6—C3—N1	−179.21 (12)
N2—N1—C1—N3	0.07 (15)	C1—N1—C3—N9	173.46 (13)
C3—N1—C1—N3	177.17 (13)	N2—N1—C3—N9	−9.7 (2)
N1—N2—C2—N3	−0.31 (16)	C1—N1—C3—N6	−7.3 (2)
N1—N2—C2—N5	177.73 (12)	N2—N1—C3—N6	169.55 (12)
C1—N3—C2—N2	0.36 (16)		

Table S2. Band angles and dihedral angles for the structure of **3**.

H05A—O5—H05B	108.2(17)	C7—N21—H21A	119.1(10)
C1—N1—C2	101.89(9)	C7—N21—H21B	122.8(10)
C2—N2—N3	99.99(8)	H21A—N21—H21B	118.1(14)
C1—N3—N2	110.44(8)	C8—N22—H22A	121.5(9)
C1—N3—C3	128.50(9)	C8—N22—H22B	118.3(10)
N2—N3—C3	121.01(8)	H22A—N22—H22B	119.8(14)
C1—N4—H4A	121.3(9)	C8—N23—H23A	118.5(10)
C1—N4—H4B	121.1(10)	C8—N23—H23B	118.8(10)
H4A—N4—H4B	117.6(13)	H23A—N23—H23B	122.6(14)
O2—N5—O1	125.35(9)	C8—N24—H24A	117.8(10)
O2—N5—C2	118.10(9)	C8—N24—H24B	119.9(10)
O1—N5—C2	116.55(9)	H24A—N24—H24B	121.7(14)
C3—N6—N7	103.18(9)	N4—C1—N1	127.42(10)
N8—N7—N6	109.33(9)	N4—C1—N3	123.79(10)

N7—N8—N9	110.40(9)	N1—C1—N3	108.79(9)
C3—N9—N8	102.46(9)	N2—C2—N1	118.89(9)
C4—N10—C5	101.82(9)	N2—C2—N5	119.45(9)
C5—N11—N12	100.32(9)	N1—C2—N5	121.66(9)
C4—N12—N11	110.28(8)	N6—C3—N9	114.64(9)
C4—N12—C6	128.73(9)	N6—C3—N3	122.83(9)
N11—N12—C6	120.97(9)	N9—C3—N3	122.53(9)
C4—N13—H13A	121.2(9)	N13—C4—N10	127.12(10)
C4—N13—H13B	118.8(10)	N13—C4—N12	124.01(10)
H13A—N13—H13B	118.8(13)	N10—C4—N12	108.85(9)
O3—N14—O4	125.19(11)	N11—C5—N10	118.73(10)
O3—N14—C5	116.91(10)	N11—C5—N14	119.53(10)
O4—N14—C5	117.90(9)	N10—C5—N14	121.75(9)
C6—N15—N16	103.17(9)	N15—C6—N18	114.50(10)
N17—N16—N15	109.56(9)	N15—C6—N12	123.55(10)
N16—N17—N18	109.89(10)	N18—C6—N12	121.96(10)
C6—N18—N17	102.89(9)	N20—C7—N21	120.71(10)
C7—N19—H19A	117.3(10)	N20—C7—N19	120.62(10)
C7—N19—H19B	121.7(10)	N21—C7—N19	118.67(10)
H19A—N19—H19B	120.9(13)	N24—C8—N22	120.87(11)
C7—N20—H20A	120.3(9)	N24—C8—N23	120.02(11)
C7—N20—H20B	118.7(9)	N22—C8—N23	119.10(11)
H20A—N20—H20B	120.9(12)		

C2—N2—N3—C1	0.24(11)	N8—N9—C3—N3	178.66(9)
C2—N2—N3—C3	178.05(9)	C1—N3—C3—N6	176.82(10)
C3—N6—N7—N8	−0.09(12)	N2—N3—C3—N6	−0.55(15)
N6—N7—N8—N9	−0.01(13)	C1—N3—C3—N9	−1.91(16)
N7—N8—N9—C3	0.10(12)	N2—N3—C3—N9	−179.28(9)

C5—N11—N12—C4	−0.28(11)	C5—N10—C4—N13	178.30(11)
C5—N11—N12—C6	−179.06(10)	C5—N10—C4—N12	0.16(11)
C6—N15—N16—N17	0.12(13)	N11—N12—C4—N13	−178.13(10)
N15—N16—N17—N18	−0.09(13)	C6—N12—C4—N13	0.53(18)
N16—N17—N18—C6	0.03(12)	N11—N12—C4—N10	0.07(12)
C2—N1—C1—N4	179.36(11)	C6—N12—C4—N10	178.74(10)
C2—N1—C1—N3	−0.27(11)	N12—N11—C5—N10	0.43(12)
N2—N3—C1—N4	−179.62(9)	N12—N11—C5—N14	−178.87(9)
C3—N3—C1—N4	2.78(17)	C4—N10—C5—N11	−0.39(13)
N2—N3—C1—N1	0.02(11)	C4—N10—C5—N14	178.88(10)
C3—N3—C1—N1	−177.57(9)	O3—N14—C5—N11	177.42(10)
N3—N2—C2—N1	−0.46(12)	O4—N14—C5—N11	−2.26(15)
N3—N2—C2—N5	179.98(9)	O3—N14—C5—N10	−1.85(15)
C1—N1—C2—N2	0.49(12)	O4—N14—C5—N10	178.47(10)
C1—N1—C2—N5	−179.96(9)	N16—N15—C6—N18	−0.10(13)
O2—N5—C2—N2	−4.42(14)	N16—N15—C6—N12	179.79(10)
O1—N5—C2—N2	175.82(9)	N17—N18—C6—N15	0.05(13)
O2—N5—C2—N1	176.03(9)	N17—N18—C6—N12	−179.84(10)
O1—N5—C2—N1	−3.73(14)	C4—N12—C6—N15	173.54(10)
N7—N6—C3—N9	0.17(12)	N11—N12—C6—N15	−7.92(16)
N7—N6—C3—N3	−178.66(9)	C4—N12—C6—N18	−6.58(17)
N8—N9—C3—N6	−0.17(12)	N11—N12—C6—N18	171.96(10)

Table S2. Band angles and dihedral angles for the structure of **9**.

C1—N1—C2	101.78(11)	C4—N13—H13A	116.6(15)
C2—N2—N3	99.73(10)	C4—N13—H13B	115.8(13)
C1—N3—N2	110.37(11)	H13A—N13—H13B	127(2)
C1—N3—C3	128.77(12)	C5—N14—H14A	122.1(14)

N2—N3—C3	120.85(10)	C5—N14—H14B	120.0(13)
C1—N4—H4A	118.6(14)	H14A—N14—H14B	116.1(18)
C1—N4—H4B	116.7(15)	N4—C1—N1	126.74(13)
H4A—N4—H4B	125(2)	N4—C1—N3	124.35(13)
O1—N5—O2	125.19(13)	N1—C1—N3	108.91(12)
O1—N5—C2	116.96(12)	N2—C2—N1	119.21(12)
O2—N5—C2	117.85(11)	N2—C2—N5	120.28(11)
C3—N6—N7	103.81(11)	N1—C2—N5	120.51(12)
N8—N7—N6	109.39(11)	N6—C3—N9	113.95(12)
N7—N8—N9	110.07(11)	N6—C3—N3	122.55(12)
C3—N9—N8	102.79(11)	N9—C3—N3	123.50(11)
C4—N10—C5	107.15(11)	N13—C4—N11	127.64(13)
C4—N10—H10	129.2(13)	N13—C4—N10	125.89(12)
C5—N10—H10	123.1(13)	N11—C4—N10	106.47(12)
C4—N11—N12	111.37(11)	N12—C5—N14	126.42(13)
C4—N11—H11	128.3(13)	N12—C5—N10	111.86(12)
N12—N11—H11	119.9(13)	N14—C5—N10	121.71(12)
C5—N12—N11	103.15(11)		
C2—N2—N3—C1	0.17(13)	O1—N5—C2—N1	−3.97(18)
C2—N2—N3—C3	−178.64(11)	O2—N5—C2—N1	175.59(12)
C3—N6—N7—N8	−0.05(14)	N7—N6—C3—N9	−0.11(15)
N6—N7—N8—N9	0.18(15)	N7—N6—C3—N3	−179.46(11)
N7—N8—N9—C3	−0.23(15)	N8—N9—C3—N6	0.21(15)
C4—N11—N12—C5	−0.08(14)	N8—N9—C3—N3	179.55(12)
C2—N1—C1—N4	179.95(14)	C1—N3—C3—N6	179.12(12)
C2—N1—C1—N3	0.29(14)	N2—N3—C3—N6	−2.30(18)
N2—N3—C1—N4	−179.98(13)	C1—N3—C3—N9	−0.2(2)
C3—N3—C1—N4	−1.3(2)	N2—N3—C3—N9	178.41(11)

N2—N3—C1—N1	−0.31(15)	N12—N11—C4—N13	−179.64(14)
C3—N3—C1—N1	178.38(12)	N12—N11—C4—N10	0.17(15)
N3—N2—C2—N1	0.02(15)	C5—N10—C4—N13	179.62(14)
N3—N2—C2—N5	180.00(11)	C5—N10—C4—N11	−0.19(14)
C1—N1—C2—N2	−0.20(16)	N11—N12—C5—N14	−179.02(13)
C1—N1—C2—N5	179.81(11)	N11—N12—C5—N10	−0.04(14)
O1—N5—C2—N2	176.05(12)	C4—N10—C5—N12	0.15(15)
O2—N5—C2—N2	−4.39(18)	C4—N10—C5—N14	179.18(13)

2 Theoretical study

Calculations were carried out by using the Gaussian 03 (Revision E.01) suite of programs.[3] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G**basis set,[4] and single-point energies were calculated at the MP2(full)/6-311++G**level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Geometry coordinates

The optimized structure of the following structure

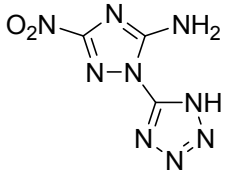


Table S4 Geometry coordinates of HANTT

C	0.2584	0.90892	-0.02081
C	-2.18677	0.62603	0.03062
N	-1.06735	1.6564	-0.01195
N	-0.04453	-0.5806	-0.09577
N	-1.55303	-0.75758	0
C	-2.22809	-1.41812	-1.12644
N	-3.73228	-1.46019	-0.89708
N	-4.17339	-2.91626	-0.9401
N	-2.94946	-3.76864	-1.24317
N	-1.73628	-2.85043	-1.277
H	-0.78395	-3.13758	-1.38
N	1.59516	1.51804	0.03344

O	1.67535	2.71334	0.09042
O	2.55221	0.79537	0.01855
N	-3.62662	0.91607	0.09071
H	-3.88517	1.12664	1.03348
H	-3.83346	1.7	-0.49467

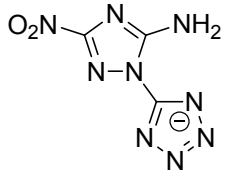
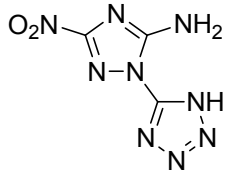
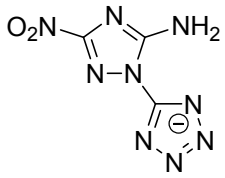
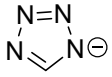
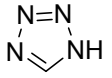


Table S5 Geometry coordinates of ANTT

C	0.2584	0.90892	-0.02081
C	-2.18677	0.62603	0.03062
N	-1.06735	1.6564	-0.01195
N	-0.04453	-0.5806	-0.09577
N	-1.55303	-0.75758	0.
C	-2.22809	-1.41812	-1.12644
N	-3.73228	-1.46019	-0.89708
N	-4.17339	-2.91626	-0.9401
N	-2.94946	-3.76864	-1.24317
N	-1.73628	-2.85043	-1.277
N	1.59516	1.51804	0.03344
O	1.67535	2.71334	0.09042
O	2.55221	0.79537	0.01855
N	-3.62662	0.91607	0.09071
H	-3.88517	1.12664	1.03348
H	-3.83346	1.7	-0.49467

Table S6. Ab Initio computional data (B3LYP/6-31+G(d,p)/MP2(full)/6-311++G**)

	E_0	ZPE	H_T	HOF ^{Exp}	HOF ^{Calcd}
	-757.737498	0.105352	0.010448		487.249784

	-757.2421329	0.092665	0.011462		293.808490
CH_4	-40.39849[a]	0.044791	0.003812	-74.6[a]	-
	-241.7583028	0.059887	0.004507	192.7[b]	
	-257.218829	0.033827	0.004225	-	170.0[c]
	-257.7256749	0.046855	0.00443	333.2[d]	-
NH_3	-56.43462[e]	0.034377	0.003818	-45.9[e]	
CH_3NO_2	-244.5543604[e]	0.049857	0.005272	-74.3[e]	
CH_3NH_2	-95.6318759[e]	0.064032	0.004369	-23.0[e]	

a Eur. J. Inorg. Chem. **2008**, 2560-2568;

b http://www.nist.gov/

c Data calculated with the G2 method by using the Gaussian 03 program.

d New J. Chem., **2008**, 32, 317-322

e Eur. J. Inorg. Chem. **2008**, 2560-2568

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3 Gaussian 03, Revision E.01, M. J.Frisch, G. W.Trucks, H. B.Schlegel, G. E.Scuseria, M. A.Robb, J. R.Cheeseman, J. A.Montgomery, J. 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, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

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