Supporting Information for

1,1'-Diamino-5,5'-Azotetrazole: A Nitrogen Rich Compound

Fang Li, Xiaomin Cong, Zhiming Du, Chunlin He, Linshuang Zhao, Lingqiao Meng*

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

Email:duzhiming430@sohu.com

Table of Contents

Experimental Section

Caution! The prepared 1,1'-diamino-5,5'-azotetrazole and its starting materials are energetic compounds with increased sensitivities against heat, impact and friction. Although we had no problems in synthesis, proper protective measures (earthen equipment, face shield and leather gloves)should be used.

General methods: All the reagents were analytical reagents purchased from commercial sources. 1,5-diaminotetrazole (DAT)[1] was synthesized by literature method. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz (Bruker DRX 500) Nuclear Magnetic Resonance spectrometers, by using DMSO[D$_6$] as solvent. The melting and decomposition points were obtained on a Differential Scanning Calorimeter (TGA/DSC 1, STAR^e System and CDR-4P) at a scan rate of 5 or 10 °C· min^{-1}. IR spectra were recorded using KBr pellets for solids on Nicolet 6700 FT-IR spectrometer. Mass spectra (ZAB-HS) were measured by using solid probe insertion (EI). Elemental analyses were carried out using an vario EL elemental analyzer. Details of the x-ray diffraction analysis of compounds **1**, **2** and **3** are provided. Data were collected on a Rigaku diffractometer equipped with a Saturn 70 CCD detector.

1. J. C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C.J. Rohbogner, M. Suter, J. J. Weigand. *Inorg. Chem.* 2005, **44**, 4237.

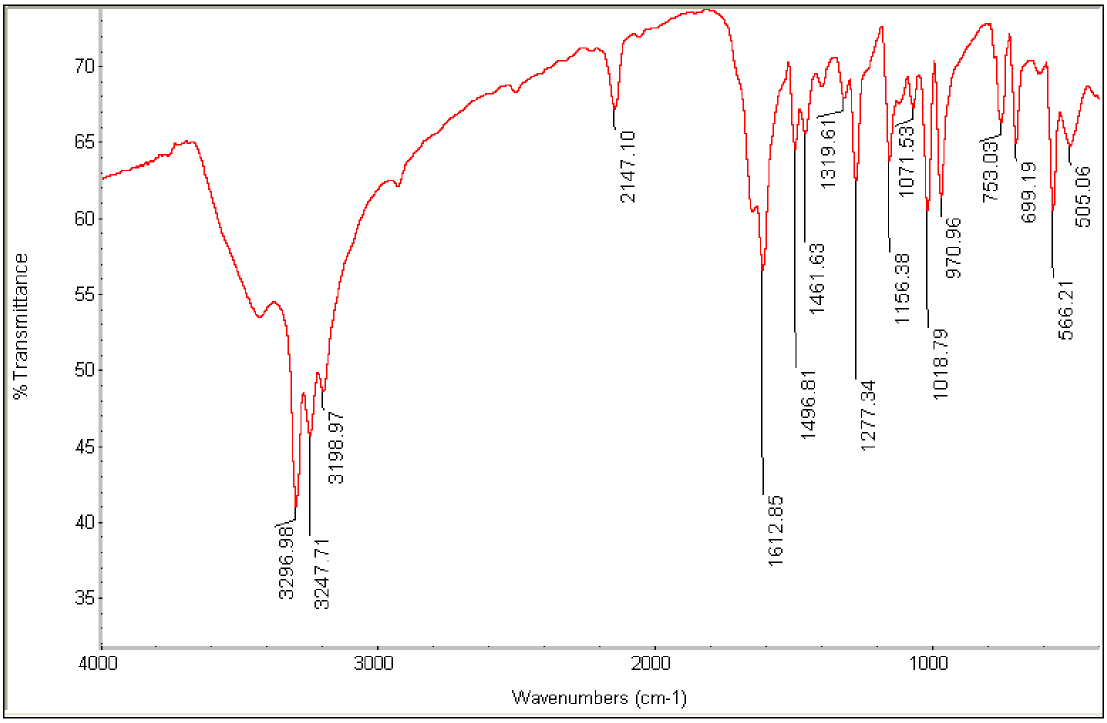


Figure 1S. Infra-red spectra of **1** was recorded by a Nicolet 6700 FT-IR spectrometer.

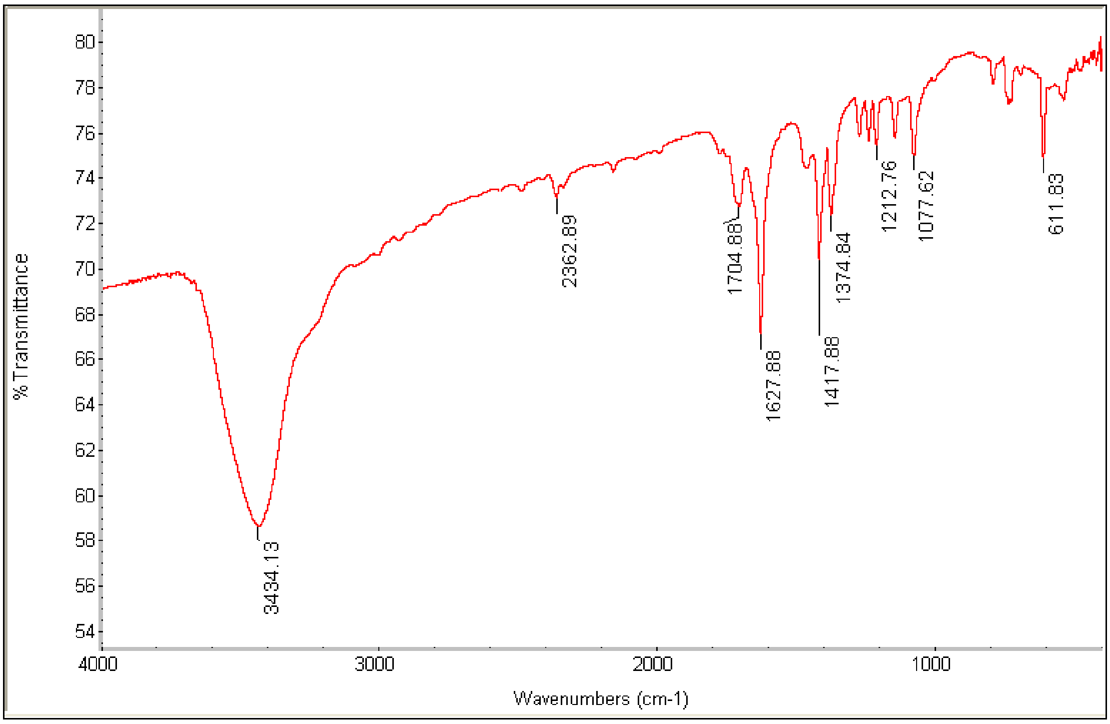


Figure 2S. Infra-red spectra of **2** was recorded by a Nicolet 6700 FT-IR spectrometer.

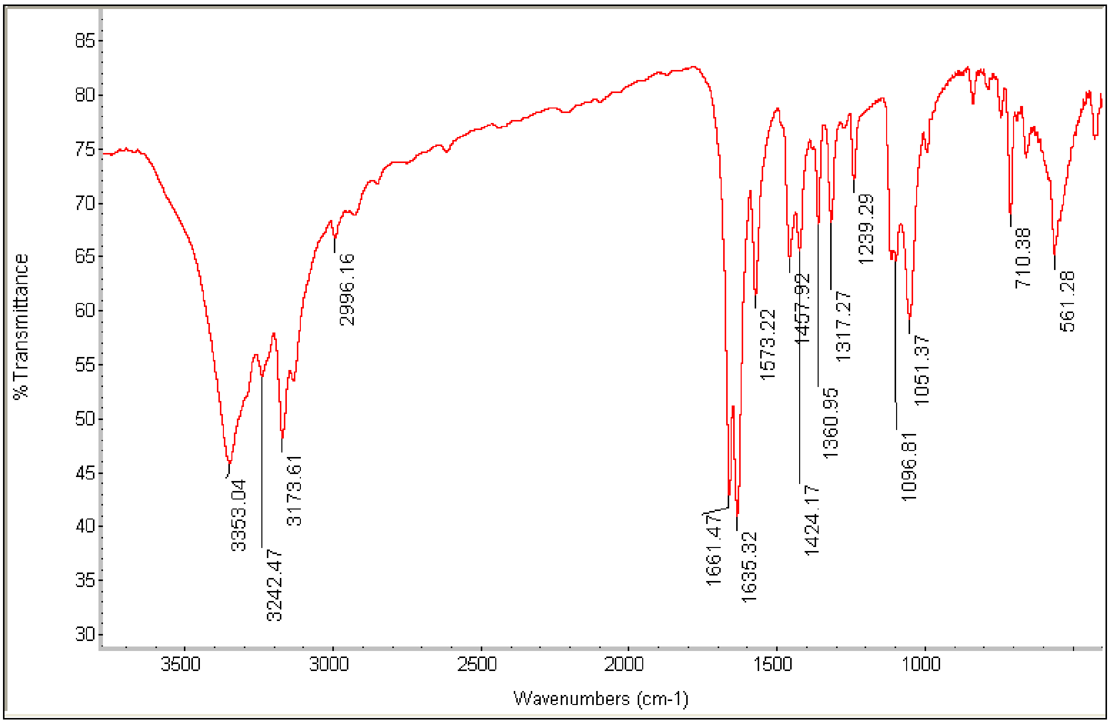


Figure 3S. Infra-red spectra of **3** was recorded by a Nicolet 6700 FT-IR spectrometer.

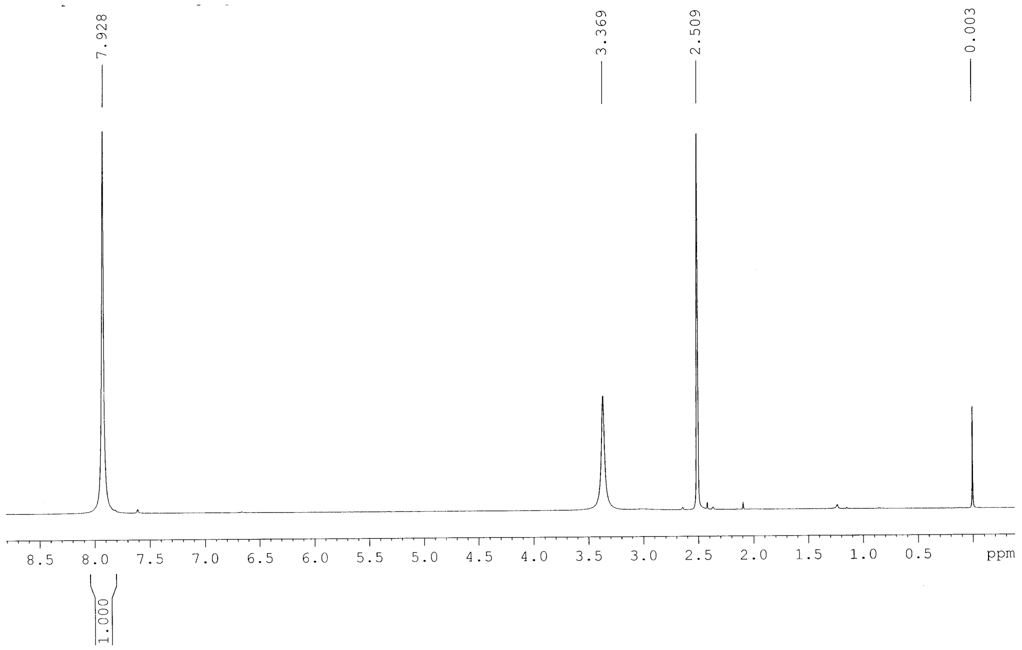


Figure 4S. ^{1}H NMR spectrum (500 MHz) of **1** in DMSO-d_6 at 25 ℃

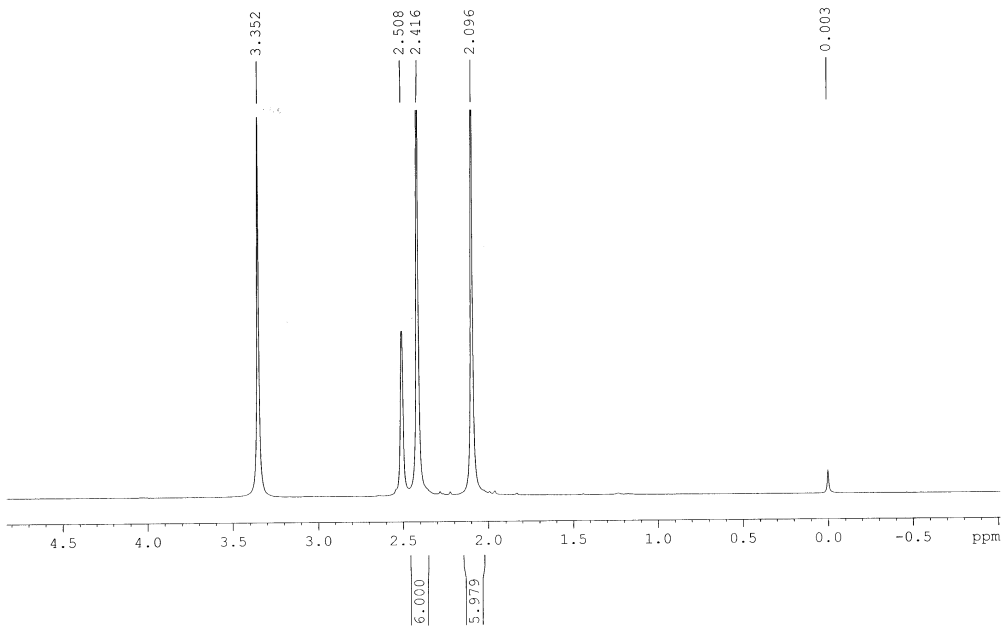


Figure 5S. ^{1}H NMR spectrum (500 MHz) of **2** in DMSO-d_6 at 25 ℃

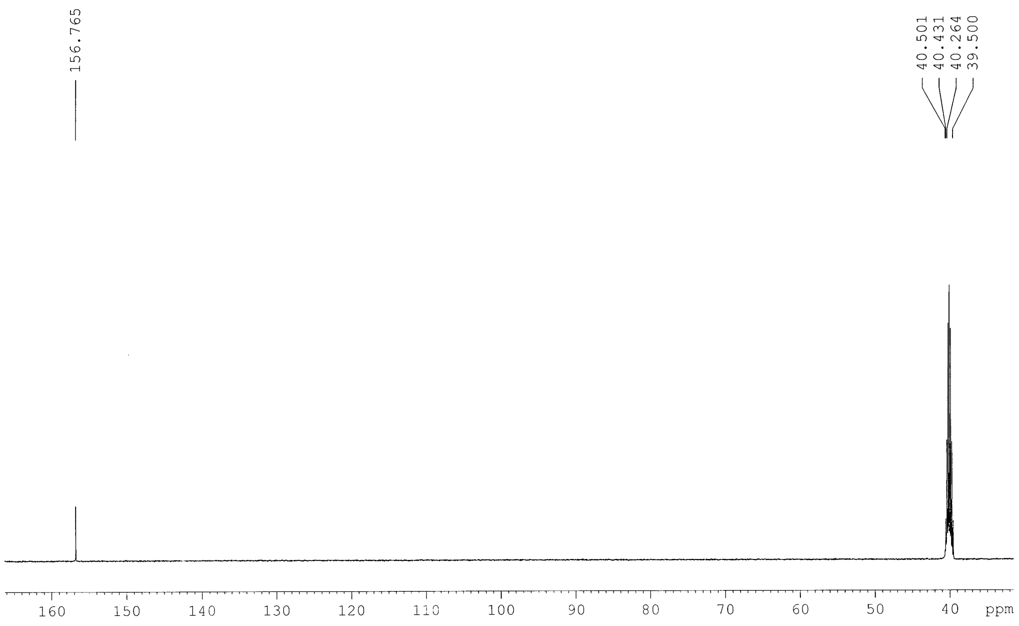
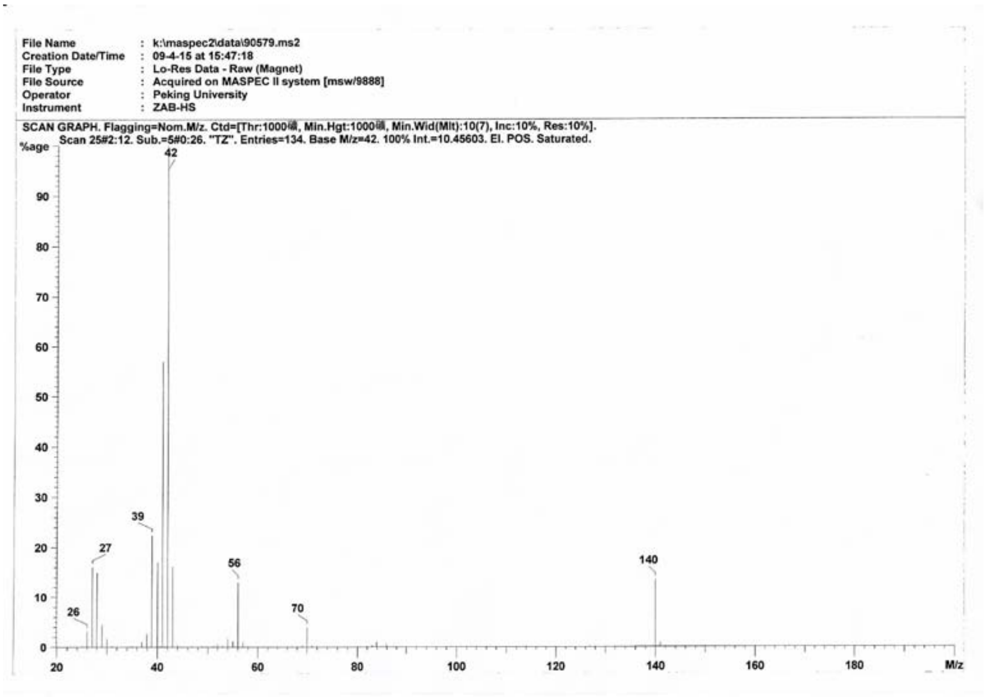


Figure 6S. ^{13}C NMR spectrum (125 MHz) of **1** in DMSO-d_6 at 25 ℃

Figure 7S. ^{13}C NMR spectrum (125 MHz) of **2** in DMSO-d_6 at 25 ℃



File Name : k:\maspec2\data\90579.ms2
Creation Date/Time : 09-4-15 at 15:47:18
File Type : Lo-Res Data - Raw (Magnet)
File Source : Acquired on MASPEC II system [msw/9888]
Operator : Peking University
Instrument : ZAB-HS

SCAN GRAPH. Flagging=Nom.M/z. Ctd=[Thr:1000, Min.Hgt:1000, Min.Wid(Mlt):10(7), Inc:10%, Res:10%].
Scan 25#2:12. Sub.=5#0:26. "TZ". Entries=134. Base M/z=42. 100% Int.=10.45603. EI. POS. Saturated.

Figure 8S. EI-MS of **1**

Thermal Analysis

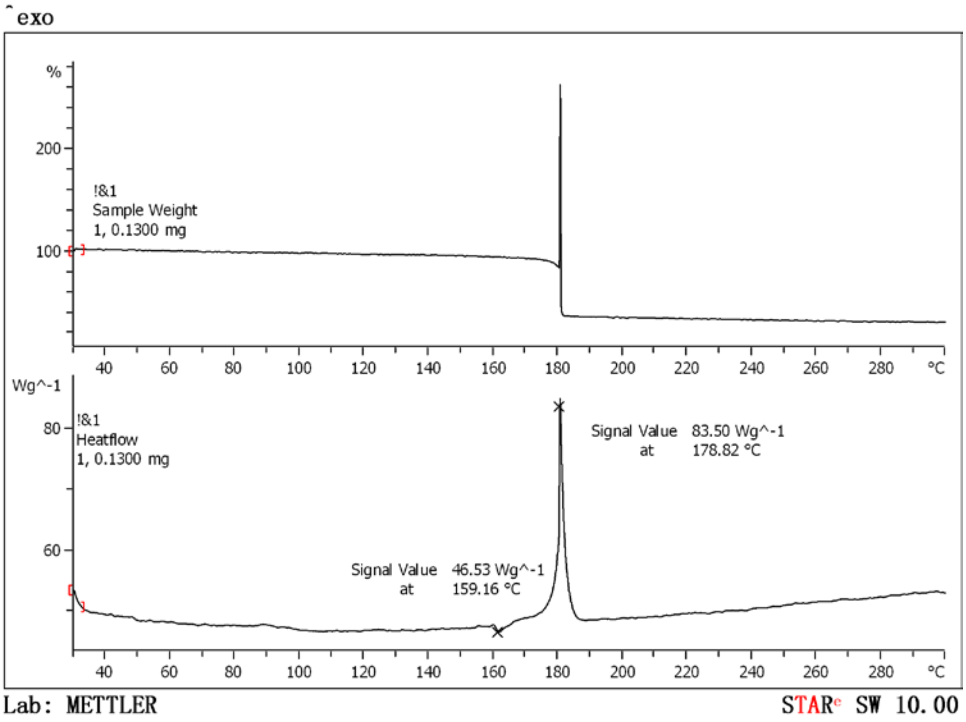


Figure 9S. DSC-TG curves of **1** carried out with a heating rate of 5℃min^{-1} in a dynamic nitrogen atmosphere.

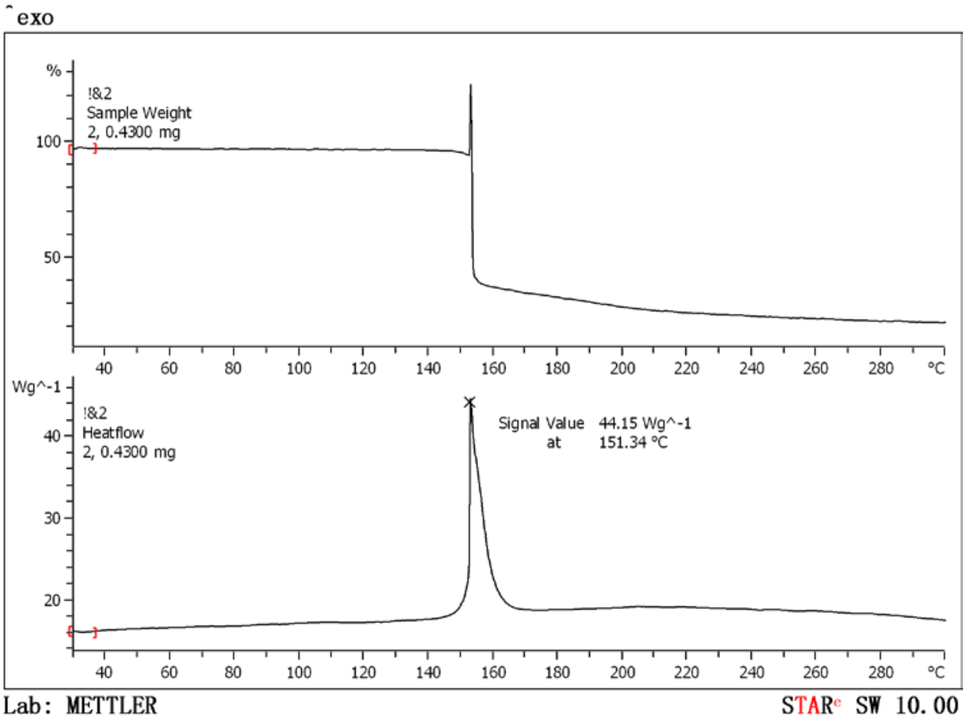


Figure 10S. DSC-TG curves of **2** carried out with a heating rate of 10℃min^{-1} in a dynamic nitrogen atmosphere.

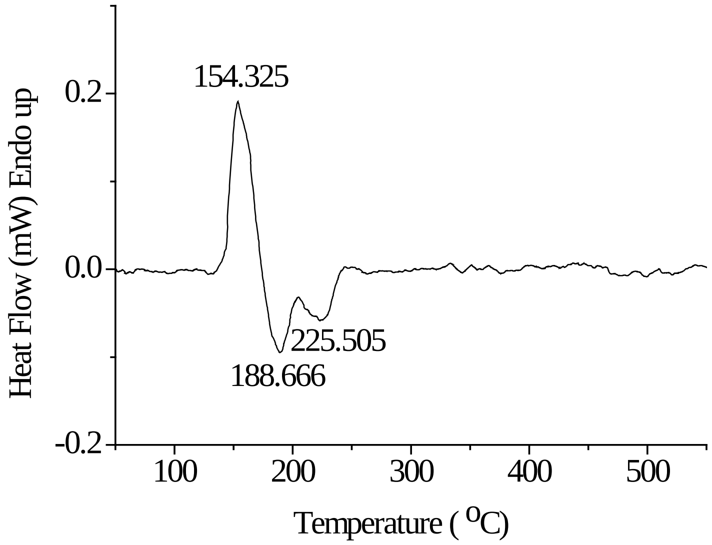


Figure 11S. DSC-TG curves of **3** carried out with a heating rate of 10℃min^{-1} in a dynamic nitrogen atmosphere.

X-ray Structural Analysis of 1

Single crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization from DMSO at room temperature.

The crystals structure data were collected by Rigaku diffractometer equipped with a Saturn 70 CCD using graphite monochromatic Mo Kα radiation (λ= 0.071073 nm) at 153(2) K in the φ and ω scans mode. Unit cell parameters were measured by least-squares methods in the range of 3.6° <θ< 31.0°, respectively. Empirical absorption corrections were applied using the Crystal-Clear program[1]. The structure was solved by the direct methods using SHELXS-97 and refined by means of full-matrix least-squares procedures on F2 with SHELXL-97 program[2].

Please see their CIF files.

Table 1S. Crystal data and refinement for **1**

Empirical formula	$C_2H_4N_{12}$
Formula weight(g/mol)	196.17
Temperature(K)	153(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size(mm)	0.51×0.38×0.23
a(Å)	6.485(4)
b(Å)	5.583(3)
c(Å)	10.854(6)
β(°)	90.786(8)
V(Å^3)	393.0(4)
Z	2
ρ_{calcd}(g /cm^3)	1.658
F(000)	200
λ(*Mo Kα*)(Å)	0.71073
θ(°)	3.0-31.0
Independent reflections	1244
R_{int}	0.024
$h/k/l$	$-9 \le h \le 9$
	$-8 \le k \le 8$
	$-15 \le l \le 11$
S	1.0
wR_2	0.087

1. G. Sheldrick. *Acta Crystallogr.* 2008, **A64**, 112.
2. G. M. Sheldrick. SHELXTL, *Structure Determination Software Programs*, Bruker Analytical of X-ray System, Inc., Madison, WI, USA, 1997.

Table 2S. Bond lengths and angles for **1**

N6—N6^i	1.2564 (18)	C1—N1—N2	104.84 (9)
N6—C1	1.3973 (15)	N1—C1—N4	109.37 (10)
N3—N2	1.3104 (14)	N1—C1—N6	130.90 (10)
N3—N4	1.3350 (14)	N4—C1—N6	119.73 (9)
N4—C1	1.3400 (14)	N3—N2—N1	111.36 (9)
N4—N5	1.3930 (13)	N2—N3—N4—C1	−0.15 (12)
N5—H5A	0.899 (18)	N2—N3—N4—N5	179.95 (10)
N5—H5B	0.89 (2)	N2—N1—C1—N4	−0.05 (12)
N1—C1	1.3207 (14)	N2—N1—C1—N6	179.54 (11)
N1—N2	1.3540 (14)	N3—N4—C1—N1	0.13 (12)
N6^i—N6—C1	112.07 (11)	N5—N4—C1—N1	−179.98 (10)
N2—N3—N4	105.98 (9)	N3—N4—C1—N6	−179.52 (9)
N3—N4—C1	108.45 (9)	N5—N4—C1—N6	0.38 (16)
N3—N4—N5	124.84 (9)	N6^i—N6—C1—N1	2.37 (19)
C1—N4—N5	126.71 (10)	N6^i—N6—C1—N4	−178.07 (11)
N4—N5—H5A	108.1 (11)	N4—N3—N2—N1	0.12 (13)
N4—N5—H5B	106.5 (12)	C1—N1—N2—N3	−0.04 (13)
H5A—N5—H5B	110.9 (16)		

Symmetry codes: (i) −x+1, −y, −z

X-ray Structural Analysis of 2

Single crystals of **2** suitable for X-ray crystallographic analysis were obtained by recrystallization from ethanol at room temperature.

The crystals structure data were collected by Rigaku diffractometer equipped with a Saturn 70 CCD using graphite monochromatic Mo Kα radiation (λ= 0.071073 nm) at 153(2) K in the φ and ω scans mode. Unit cell parameters were measured by least-squares methods in the range of 2.6° <θ< 29.1°, respectively. Empirical absorption corrections were applied using the Crystal Clear program[1]. The structure was solved by the direct methods using SHELXS-97 and refined by means of full-matrix least-squares procedures on F2 with SHELXL-97 program[2].

Please see their CIF files.

Table 3S. Crystal data and refinement for **2**

Empirical formula	$C_8H_{12}N_{12}$
Formula weight(g/mol)	276.30
Temperature(K)	153(2)
Crystal system	Monclinic
Space group	$P2_1/c$
Crystal size(mm)	0.24×0.24×0.13
a(Å)	8.661(3)
b(Å)	8.102(2)
c(Å)	10.043(3)
β(°)	115.001(3)
V(Å^3)	638.6(3)
Z	2
ρ_{calcd}(g /cm^3)	1.437
F(000)	288
λ(*Mo Kα*)(Å)	0.71073
θ(°)	2.6-29.1
Independent reflections	1683
R_{int}	0.022
$h/k/l$	$-11\leq h\leq 11$ $-11\leq k\leq 6$ $-13\leq k\leq 13$
S	1.0
wR_2	0.101

1. G. Sheldrick. *Acta Crystallogr.* 2008, **A64**, 112.
2. G. M. Sheldrick. SHELXTL, *Structure Determination Software Programs*, Bruker Analytical of X-ray System, Inc., Madison, WI, USA, 1997.

Table 4S. Bond lengths and angles for **2**

N1—C1	1.3241 (15)	N1—C1—N6	131.86 (10)
N1—N2	1.3479 (14)	N4—C1—N6	119.27 (9)
N2—N3	1.3169 (14)	N5—C2—C3	114.81 (11)
N3—N4	1.3337 (13)	N5—C2—C4	126.24 (10)
N4—C1	1.3474 (15)	C3—C2—C4	118.95 (10)
N4—N5	1.4129 (13)	C2—C3—H3A	109.5
N5—C2	1.2839 (15)	C2—C3—H3B	109.5
N6—N6i	1.2631 (19)	H3A—C3—H3B	109.5
N6—C1	1.3971 (14)	C2—C3—H3C	109.5
C2—C3	1.4916 (16)	H3A—C3—H3C	109.5
C2—C4	1.4933 (16)	H3B—C3—H3C	109.5
C3—H3A	0.9800	C2—C4—H4A	109.5
C3—H3B	0.9800	C2—C4—H4B	109.5
C3—H3C	0.9800	H4A—C4—H4B	109.5
C4—H4A	0.9800	C2—C4—H4C	109.5
C4—H4B	0.9800	H4A—C4—H4C	109.5
C4—H4C	0.9800	H4B—C4—H4C	109.5
C1—N1—N2	105.25 (9)	C1—N1—N2—N3	−0.36 (12)
N3—N2—N1	111.45 (9)	N1—N2—N3—N4	0.68 (13)
N2—N3—N4	105.78 (10)	N2—N3—N4—C1	−0.73 (12)
N3—N4—C1	108.68 (9)	N2—N3—N4—N5	−170.58 (9)
N3—N4—N5	121.23 (10)	N3—N4—C1—N1	0.53 (12)
C1—N4—N5	129.16 (9)	N5—N4—C1—N1	169.33 (10)
C2—N5—N4	113.98 (9)	N3—N4—C1—N6	179.04 (9)
N6i—N6—C1	112.07 (11)	N5—N4—C1—N6	−12.16 (16)
N1—C1—N4	108.84 (10)		

Symmetry codes: (i) −x+1, −y+1, −z+1.

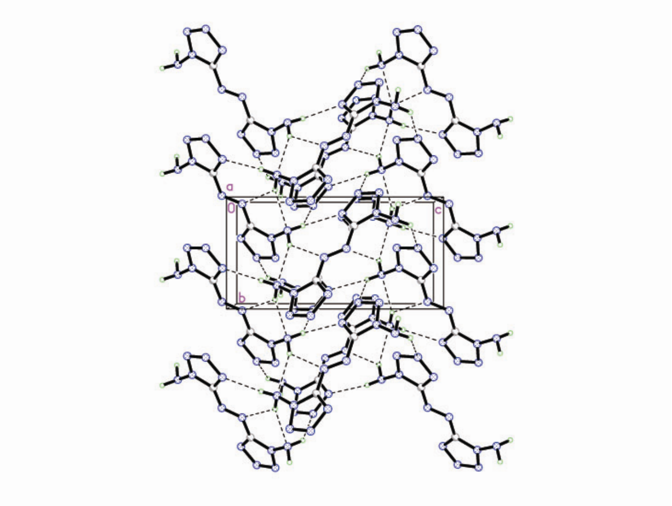


Figure 12S. Packing diagram of **1** viewed down the a-axis.

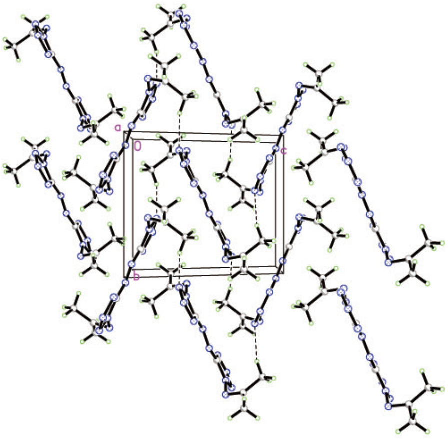


Figure 13S. Packing diagram of **2** viewed down the a-axis.

X-ray Structural Analysis of 3

Single crystals of **3** suitable for X-ray crystallographic analysis were obtained by recrystallization from water at room temperature.

The crystals structure data were collected by Rigaku diffractometer equipped with a Saturn 70 CCD using graphite monochromatic Mo Kα radiation (λ= 0.071073 nm) at 153(2) K in the φ and ω scans mode. Unit cell parameters were measured by least-squares methods in the range of 2.7° <θ< 29.1°, respectively. Empirical absorption corrections were applied using the Crystal Clear program[1]. The structure was solved by the direct methods using SHELXS-97 and refined by means of full-matrix least-squares procedures on F2 with SHELXL-97 program[2].

Please see their CIF files.

Table 5S. Crystal data and refinement for **3**

Empirical formula	$C_4H_8N_6$
Formula weight(g/mol)	140.16
Temperature(K)	153(2)
Crystal system	Monoclinic
Space group	$P2_1$/C
Crystal size(mm)	0.22×0.19×0.11
a(Å)	7.533(3)
b(Å)	7.408(2)
c(Å)	12.029(4)
β(°)	96.629(4)
V(Å^3)	666.8(4)
Z	4
ρ_{calcd}(g /cm^3)	1.396
F(000)	296
λ(*Mo Kα*)(Å)	0.71073
θ(°)	2.7-29.1
Independent reflections	1768
R_{int}	0.029
h/*k*/*l*	$-10 \le h \le 10$ $-9 \le k \le 10$ $-16 \le l \le 16$
S	1.0
wR_2	0.088

1. G. Sheldrick. *Acta Crystallogr.* 2008, **A64**, 112.
2. G. M. Sheldrick. SHELXTL, *Structure Determination Software Programs*, Bruker Analytical of X-ray System, Inc., Madison, WI, USA, 1997.

Table 6S. Bond lengths and angles for **3**

N1—C1	1.3325 (16)	N1—C1—N4	108.17 (11)
N1—N2	1.3668 (16)	N5—C2—C3	114.43 (12)
N2—N3	1.2867 (16)	N5—C2—C4	128.51 (12)
N3—N4	1.3801 (15)	C3—C2—C4	117.06 (12)
N4—C1	1.3511 (17)	C2—C3—H3A	109.5
N4—N5	1.3873 (14)	C2—C3—H3B	109.5
N5—C2	1.2820 (17)	H3A—C3—H3B	109.5
N6—C1	1.3283 (18)	C2—C3—H3C	109.5
N6—H6A	0.894 (18)	H3A—C3—H3C	109.5
N6—H6B	0.892 (18)	H3B—C3—H3C	109.5
C2—C3	1.4942 (19)	C2—C4—H4A	109.5
C2—C4	1.495 (2)	C2—C4—H4B	109.5
C3—H3A	0.9800	H4A—C4—H4B	109.5
C3—H3B	0.9800	C2—C4—H4C	109.5
C3—H3C	0.9800	H4A—C4—H4C	109.5
C4—H4A	0.9800	H4B—C4—H4C	109.5
C4—H4B	0.9800	C1—N1—N2—N3	0.41 (15)
C4—H4C	0.9800	N1—N2—N3—N4	−0.08 (15)
C1—N1—N2	105.50 (11)	N2—N3—N4—C1	−0.28 (14)
N3—N2—N1	112.53 (11)	N2—N3—N4—N5	178.19 (12)
N2—N3—N4	105.20 (11)	C1—N4—N5—C2	177.07 (12)
C1—N4—N3	108.60 (10)	N3—N4—N5—C2	−1.2 (2)
C1—N4—N5	120.70 (11)	N2—N1—C1—N6	179.94 (14)
N3—N4—N5	130.69 (11)	N2—N1—C1—N4	−0.57 (14)
C2—N5—N4	120.94 (11)	N3—N4—C1—N6	−179.95 (13)
C1—N6—H6A	116.5 (11)	N5—N4—C1—N6	1.4 (2)
C1—N6—H6B	120.7 (11)	N3—N4—C1—N1	0.54 (14)
H6A—N6—H6B	122.7 (15)	N5—N4—C1—N1	−178.11 (11)
N6—C1—N1	127.06 (13)	N4—N5—C2—C3	−179.42 (12)
N6—C1—N4	124.77 (12)	N4—N5—C2—C4	1.3 (2)

Table 7S. Hydrogen bonds for **3**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6A···N1^{i}	0.894(18)	2.108(19)	2.9799(19)	164.6(15)
N6—H6B···N2^{ii}	0.892(18)	2.209(18)	3.0688(19)	161.6(15)

Symmetry codes: (i) -x, -y+2, -z+1−; (ii) x, -y+3/2, z-1/2;

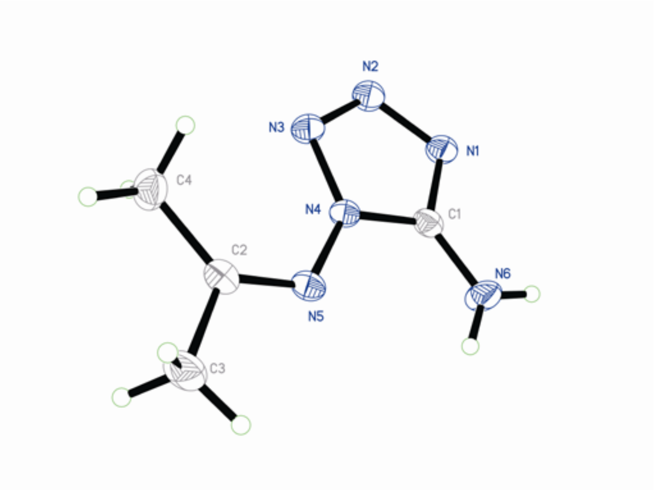


Figure 14S. 1,1’-diisopropylideneamino -5,5’-azotetrazole

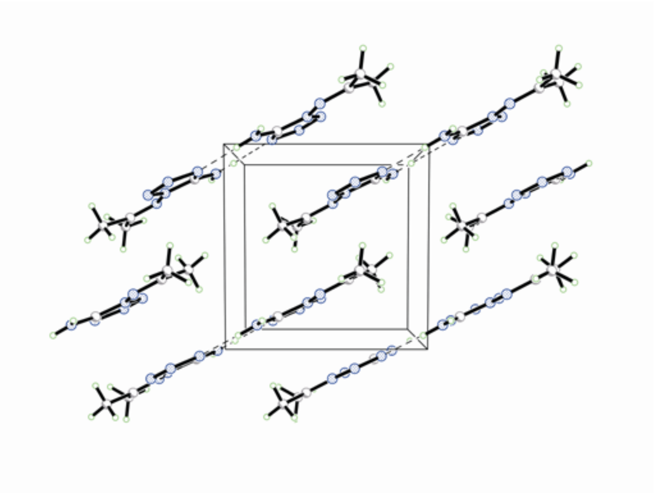


Figure 15S. Packing diagram of **3** viewed down the c-axis.

Computation details

The heats of formation for **1** and **2** were calculated using Gaussian 03.[1] The geometric optimization of structures and frequency analyses were using the B3LYP[2-5] with the 6-31+G** basis set[6], and single-point energies were calculated at the MP2/6-311++G** level.[7,8] Heats of formation for simple molecules were determined by using atomization energies at G2 level.[9] The whole optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The heats of formation for **1** and **2** were determined by using the methods of isodesmic reactions.[10-12]

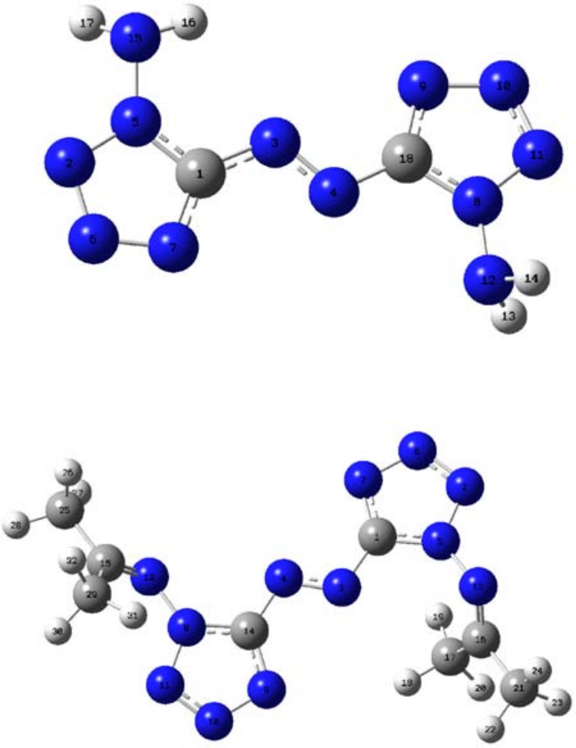


Figure 16S. The optimized structure of **1** and **2** at B3LYP with the 6-31+G** level.

Table 8S. Cartesian coordinates of the optimized structure **1**

1	X	Y	Z
C1	1.665798	1.185283	0.024039
N2	3.596151	2.199577	0.215063
N3	0.820535	0.091288	0.050287
N4	-0.393102	0.35761	-0.175254
N5	2.991555	1.012651	0.298461
N6	2.667844	3.059512	-0.145347
N7	1.470587	2.470903	-0.262774
N8	-2.55233	-0.652015	-0.280788
N9	-0.903344	-2.067681	-0.133469
N10	-2.073682	-2.719671	-0.215503
N11	-3.082194	-1.888882	-0.305787
N12	-3.258422	0.513614	-0.555016
N13	3.653586	-0.080251	0.86602
C14	-1.200947	-0.771162	-0.188623
C15	-4.328182	0.727165	0.133612
C16	3.797562	-1.116668	0.111969
C17	3.374847	-1.261303	-1.323286
H18	2.415055	-1.789968	-1.361348
H19	3.259053	-0.299915	-1.826798
H20	4.10853	-1.864049	-1.86568
C21	4.455663	-2.299153	0.761794
H22	3.795531	-3.171827	0.6949
H23	5.380371	-2.551545	0.230181
H24	4.681019	-2.092186	1.808603
C25	-5.094193	1.963053	-0.241728
H26	-5.135855	2.648545	0.612876
H27	-4.629407	2.467288	-1.089656
H28	-6.128698	1.699819	-0.49254
C29	-4.873643	-0.114646	1.25534
H30	-5.588744	-0.843472	0.857405
H31	-4.09467	-0.676494	1.77341
H32	-5.403908	0.521804	1.968692

Table 9S. Cartesian coordinates of the optimized structure **2**

2	*X*	*Y*	*Z*
C1	-1.745169	-0.257893	-0.007005
N2	-3.930962	-0.168743	-0.010432
N3	-0.496361	0.320906	0.007269
N4	0.476978	-0.482568	-0.000222
N5	-2.827893	0.562632	0.049004
N6	-3.523976	-1.424981	-0.1248
N7	-2.195033	-1.512207	-0.114516
N8	2.866683	-0.544248	0.041245
N9	2.017662	1.449551	-0.130957
N10	3.366321	1.509155	-0.123074
N11	3.894975	0.322245	-0.019223
N12	3.015054	-1.920171	0.168295
H13	3.505037	-2.271092	-0.651629
H14	3.571767	-2.107861	0.998966
N15	-2.862444	1.932492	0.272674
H16	-1.924899	2.293127	0.097469
H17	-3.538243	2.343533	-0.367771
C18	1.708385	0.163535	-0.023642

Scheme 1S. Isodesmic Reactions for compounds **1** and **2**.

Table 10S. The heat of formation (HOF) for compounds **1** and **2**

Compd.	**E_0/a.u.**	**ZPE(kJ/mol)**	**H_T(kJ/mol)**	**HOF(kJ/mol)**
1	-733.7135235	0.116197	0.129030	429.0
2	-966.4952923	0.235635	0.255871	424.2

1. The impact and friction sensitivity of **1** and **2** were determined (Table 12S). The test result (H_{50}) are <4 cm and 20.6 cm, which measured by a falling hammer, 2 kg and 5 kg weight are dropped from a setting height onto a 30 mg sample of an explosive placed on 150 grit garnet sandpaper. The friction sensitivity is measured by a 1.5 kg weight hammer which is hit from 70°switch angle onto a 20 mg sample of an explosive place with 1.96 MPa. 50 samples are made respectively and an explosion or nonexplosion is recorded. The results were listed using explosion probability method. Under the same test condition, the greater explosion probability is, the higher the sensitivity is.

Table 11 S. The properties of compound **1** and **2.**

Compd.	***1***	***2***
P(GPa)[a]	33.04	21.65
D($km\cdot s^{-1}$)[b]	8.723	7.396
H_{50}(cm)[c]	<4	20.6
F(%)	100%	100%

Note：[a]Detonation pressure. [b]Detonation velocity.[c]Impact sensitivity

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr., J. A. Montgomery, 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. K Li, X. lene, 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, Z V.G. akrzewski, 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. tefanov, 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.
2 A. D. Becke. *Phys. Rev. A.* 1988, **38**, 3098-3100.
3 C. Lee, W. Yang, R. G. Parr. *Phys. Rev.* 1988, **B37**, 785-789.
4 A. Becke. *J. Chem. Phy.* 1993, **98**, 5648-5652.
5 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch. *J. Phy. Chem.* 1994, **98**, 11623-11627.
6 R. G. Parr, W. Yang. *Density-functional theory of atoms and molecules,* Oxford University Press ; Clarendon Press, New York Oxford England, 1989.
7 J. A. Pople, J. S. Binkley, R. Seeger. *Int. J. Quantum Chem.* 1976, **10**, 1-19.
8 C. M. Aikens, S. P. Webb, R. L. Bell, G. D. Fletcher, M. W. Schmidt, M. S. Gordon. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta),* 2003, **110**, 233-253.
9 L. A. Curtiss, K. G. Raghavachari, W. Trucks, J. A. Pople,. *J. Chem. Phy.* 1991, **94**, 7221-7230.
10 H. D. B. Jenkins, D. Tudela, L. Glasser. *Inorg. Chem.* 2002, **41**, 2364-2367.
11 M. W. Schmidt, M. S. Gordon, J. A. Boatz. *J. Phys. Chem A,* 2005, **109**, 7285-7295.
12 H. X. Gao, C. F. Ye, C. M. Piekarski, J. M. Shreeve. *J. Phys. Chem C.* 2007, **111**, 10718-10731.