

3-Amino-6-nitroamino-tetrazine (ANAT)-Based Energetic Salts

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Electronic supplementary information

S -1-4 - Experimental Details

S – 4-11 - Crystallographic details and packing diagram from crystal structure of guanidine ANAT

S – 12 – 14 -. *Ab Initio* computational details for optimization of the ANAT anion

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Caution: While we have experienced no difficulties with shock and friction sensitivity of these compounds with high nitrogen content and rather high heats of formation, they should be synthesized in mmole amounts and handled with extreme care.

General Methods. All the reagents used were analytical grade purchased from commercial sources and used as received. ANAT was prepared according to the literature by the nitration of 3-6-diamino-tetrazine with nitric acid at room temperature in 73 % yield.¹ 3,6-Diguanidinium tetrazine² and 1,2,3-triamino guanidine³ were synthesized by the literature methods. ¹H and ¹³C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. Chemical shifts were reported relative to Me₄Si. The solvent was DMSO-*d*₆ unless otherwise specified. The melting and decomposition points were recorded on a

differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C/min, respectively. IR spectra were recorded using KBr pellets. The densities of energetic salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were performed in house on an EXETER CE-440 Elemental Analyzer.

Synthesis

3,6-Diguanidinium tetrazine di(ANAT) (2). ANAT (157mg, 1mmol) and 3,6-diguanidinium tetrazine (255 mg, 0.5mmol) were placed in water (5 ml). After stirring at 60 °C for 3 hours, followed by cooling to room temperature, a microcrystalline solid was isolated. Orange needle crystals were obtained upon recrystallization from water (370 mg, 90%). IR (KBr pellet): 3406, 3287, 3194, 2361, 1702, 1630, 1601, 1506, 1426, 1377, 1304, 1150, 1070, 1032, 949, 851, 770, 659, 568, 493 cm⁻¹. ¹H NMR δ7.81 (s,4H), 7.61 (s,8H); ¹³C NMR (D₂O): δ163.3,161.4, 160.8, 157.6. Anal. Calcd for C₈H₁₄N₂₄O₄ (510.4): C, 18.83; H, 2.76; N, 65.87; Found: C, 18.84; H, 2.46; N, 65.44.

Guanidine ANAT (3). ANAT (157mg, 1 mmol) and guanidine carbonate (90.9 mg, 0.5mmol) was added in water (5 ml). After CO₂ release was completed and the solution was stirred at room temperature for 3 hours, the solvent was slowly removed, and the product isolated as a microcrystalline solid (220 mg, 93%). Orange crystals suitable for X-ray diffraction were obtained upon recrystallization from water. IR (KBr pellet): 3414, 3327, 3201, 2429, 2331, 2252, 1681, 1630, 1523, 1467, 1433, 1367, 1295, 1163, 1062, 968, 898, 667, 465, 421 cm⁻¹. ¹H NMR 7.45 (s,2H), 6.99 (s,6H). ¹³C NMR (D₂O): δ164.9, 163.0, 159.2. Anal. Calcd for C₃H₈N₁₀O₂ (216.2.): C, 16.67; H, 3.73; N, 64.80; Found: C, 16.65; H, 3.63; N, 64.55.

Aminoguanidinium ANAT (4). After a mixture of *ANAT* (157mg, 1 mmol) and amino-guanidinium bicarbonate (136mg, 1mmol) in water (10 ml) was stirred for 3 hours, and the solvent removed, the product was isolated as red plate crystals. (270 mg, 92%). IR (KBr pellet): 3461, 3169, 3077, 2435, 2362, 1676, 1612, 1509, 1463, 1425, 1371, 1304, 1215, 1125, 1064, 1024, 950, 890, 768, 703, 662, 615, 577, 524, 416 cm^{-1} . ^1H NMR δ 8.63 (s,1H), 7.38 (s,2H), 7.23 (s, br, 2H), 6.89 (s, br,2H), 4.68 (s,2H). ^{13}C NMR (D_2O): δ 164.9, 163.0, 160.2. Anal. Calcd for $\text{C}_3\text{H}_9\text{N}_{11}\text{O}_2$ (231.2): C, 15.59; H, 3.92; N, 66.65; Found: C, 15.57; H, 3.67; N, 66.23.

Ammonium ANAT (5). *ANAT* (157mg, 1 mmol) in water (5 ml) and aqueous ammonia solution (1mmol) was stirred for 3 hours, and the solvent slowly removed. The product was isolated as red needle crystals (160 mg, 92%). IR (KBr pellet): 3300, 3173, 1645, 1525, 1421, 1354, 1296, 1060, 1029, 972, 883, 848, 772, 571, 480, 435 cm^{-1} . ^1H NMR δ 7.39 (s,2H), 7.20 (s,4H). ^{13}C NMR: δ 164.8, 163.0. Anal. Calcd for $\text{C}_2\text{H}_6\text{N}_8\text{O}_2$ (174.1): C, 13.80; H, 3.47; N, 64.35; Found: C, 14.16; H, 3.50; N, 64.20.

1,3-Diaminoguanidine ANAT (6). This solid was obtained via the reaction of silver *ANAT* (264 mg, 1 mmol) suspended in water (10 ml) and an aqueous solution of 1,2,3-triaminoguanidine chloride (126mg, 1mmol). After being stirred for 3 hr, the insoluble material was removed by filtration, and the solvent slowly removed. The product was isolated as a red needle crystals. (201 mg, 82%). IR (KBr pellet): 3406, 3317, 3283, 3189, 2998, 2906, 2362, 1685, 1641, 1413, 1381, 1376, 1333, 1278, 1180, 1051, 996, 939, 891, 767, 687, 665, 570 cm^{-1} . ^1H NMR δ 8.60 (2H, s,br), 7.36 (2H, s), 7.21 (2H, s,br), 4.59 (4H, s). ^{13}C NMR 165.0, 163.0, 161.2. Anal. Calcd for $\text{C}_3\text{H}_{10}\text{N}_{12}\text{O}_2$ (246.2.): C, 14.64; H, 4.09; N, 68.27; Found: C, 14.46; H, 4.07; N, 67.86.

1,2,3-Triaminoguanidine ANAT (7). Silver *ANAT* (264mg, 1 mmol) was suspended in water (10 ml) and an aqueous solution of 1,2,3-triaminoguanidine chloride (141mg, 1mmol) was added. After stirring for 3 hours, solids were removed by filtration, and the solvent was removed slowly. The product was isolated as red plates (218 mg, 84%). Red crystals suitable for X-ray diffraction were obtained upon recrystallization from water. IR (KBr pellet): 3401, 3358, 3321, 3196, 2361, 1924, 1683, 1621, 1514, 1346, 1295, 1138, 1064, 951, 886, 808, 767, 574, 522, 490, 424 cm^{-1} . ^1H NMR 8.58 (3H, s), 7.32 (2H, s), 4.49 (6H,s); ^{13}C NMR 165.2, 162.9,160.4. Anal. Calcd for $\text{C}_3\text{H}_{11}\text{N}_{13}\text{O}_2$ (261.2): C, 13.79; H, 4.24; N, 69.71; Found: C, 13.70; H, 4.09; N, 68.64.

Crystal Structure of 3

Crystals of compound **1** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.⁴ Data for **1** were collected at 89(2) K using a Bruker/Siemens SMART APEX instrument (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) 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 \AA . The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART⁵ software and refined using SAINTPlus⁶ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.⁷ The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.⁸ The structure was solved in the space group $P2(1)/c$ (#

14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1.

Table S1. Crystal data and structure refinement for C₂ H₂ N₇ O₂, C H₆ N₃.

Empirical formula	C ₃ H ₈ N ₁₀ O ₂	
Formula weight	216.19	
Temperature	89(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.155(2) Å	α = 90°.
	b = 15.305(4) Å	β = 99.895(5)°.
	c = 6.8667(18) Å	γ = 90°.
Volume	844.3(4) Å ³	
Z	4	
Density (calculated)	1.701 Mg/m ³	
Absorption coefficient	0.142 mm ⁻¹	
F(000)	448	
Crystal size	0.20 x 0.20 x 0.16 mm ³	
Crystal color and habit	orange needle	
Diffractometer	Bruker/Siemens SMART APEX	
Theta range for data collection	2.54 to 25.25°.	
Index ranges	-9<=h<=9, -18<=k<=18, -8<=l<=8	
Reflections collected	12622	
Independent reflections	1530 [R(int) = 0.0247]	
Completeness to theta = 25.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9776 and 0.9721	
Solution method	XS, Bruker SHELXTL v. 6.12	

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1530 / 0 / 136
Goodness-of-fit on F ²	1.100
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0782
R indices (all data)	R1 = 0.0340, wR2 = 0.0795
Largest diff. peak and hole	0.274 and -0.206 e.Å ⁻³

Table S2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for bt847. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	5970(2)	8154(1)	5297(2)	19(1)
N(3)	7863(2)	9271(1)	5203(2)	18(1)
N(4)	5313(2)	9312(1)	3195(2)	19(1)
O(2)	1775(1)	8967(1)	6631(2)	21(1)
O(1)	4117(1)	9081(1)	8714(2)	19(1)
C(1)	6380(2)	8908(1)	4560(2)	15(1)
C(7)	1564(2)	7301(1)	7534(2)	14(1)
C(10)	-836(2)	6276(1)	6031(2)	14(1)
N(5)	2913(2)	8622(1)	7869(2)	16(1)
N(6)	2956(2)	7792(1)	8325(2)	16(1)
N(8)	1944(2)	6477(1)	7089(2)	15(1)
N(9)	733(2)	5948(1)	6333(2)	15(1)
N(11)	-1224(2)	7045(1)	6801(2)	16(1)
N(12)	7(2)	7574(1)	7546(2)	16(1)
N(13)	-2045(2)	5793(1)	5016(2)	18(1)

Table S3. Bond lengths [Å] and angles [°] for 3.

N(2)-C(1)	1.326(2)
N(2)-H(2A)	0.8800
N(2)-H(2B)	0.8800
N(3)-C(1)	1.335(2)
N(3)-H(3A)	0.8800
N(3)-H(3B)	0.8800
N(4)-C(1)	1.318(2)
N(4)-H(4A)	0.8800
N(4)-H(4B)	0.8800
O(2)-N(5)	1.2613(16)
O(1)-N(5)	1.2639(16)
C(7)-N(12)	1.338(2)
C(7)-N(8)	1.3463(19)
C(7)-N(6)	1.3909(19)
C(10)-N(13)	1.3292(19)
C(10)-N(11)	1.3506(19)
C(10)-N(9)	1.3570(19)
N(5)-N(6)	1.3084(18)
N(8)-N(9)	1.3130(17)
N(11)-N(12)	1.3215(18)
N(13)-H(13A)	0.8800
N(13)-H(13B)	0.8800
C(1)-N(2)-H(2A)	120.0
C(1)-N(2)-H(2B)	120.0
H(2A)-N(2)-H(2B)	120.0
C(1)-N(3)-H(3A)	120.0
C(1)-N(3)-H(3B)	120.0
H(3A)-N(3)-H(3B)	120.0
C(1)-N(4)-H(4A)	120.0

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C(1)-N(4)-H(4B)	120.0
H(4A)-N(4)-H(4B)	120.0
N(4)-C(1)-N(2)	120.08(14)
N(4)-C(1)-N(3)	119.31(14)
N(2)-C(1)-N(3)	120.61(14)
N(12)-C(7)-N(8)	123.29(13)
N(12)-C(7)-N(6)	122.72(13)
N(8)-C(7)-N(6)	113.01(12)
N(13)-C(10)-N(11)	119.19(13)
N(13)-C(10)-N(9)	117.97(13)
N(11)-C(10)-N(9)	122.75(13)
O(2)-N(5)-O(1)	120.08(12)
O(2)-N(5)-N(6)	123.57(12)
O(1)-N(5)-N(6)	116.34(12)
N(5)-N(6)-C(7)	116.45(12)
N(9)-N(8)-C(7)	118.77(12)
N(8)-N(9)-C(10)	117.21(12)
N(12)-N(11)-C(10)	118.16(12)
N(11)-N(12)-C(7)	117.72(12)
C(10)-N(13)-H(13A)	120.0
C(10)-N(13)-H(13B)	120.0
H(13A)-N(13)-H(13B)	120.0

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N(2)	14(1)	19(1)	21(1)	4(1)	-1(1)	0(1)
N(3)	17(1)	17(1)	18(1)	2(1)	-1(1)	-2(1)
N(4)	15(1)	18(1)	22(1)	4(1)	0(1)	-3(1)
O(2)	21(1)	18(1)	23(1)	5(1)	-3(1)	-1(1)
O(1)	18(1)	17(1)	21(1)	-3(1)	0(1)	-5(1)
C(1)	16(1)	17(1)	14(1)	-4(1)	5(1)	1(1)
C(7)	17(1)	15(1)	11(1)	1(1)	3(1)	2(1)
C(10)	16(1)	14(1)	14(1)	4(1)	5(1)	0(1)
N(5)	16(1)	16(1)	16(1)	-1(1)	3(1)	-1(1)
N(6)	16(1)	13(1)	19(1)	-1(1)	2(1)	-1(1)
N(8)	16(1)	15(1)	15(1)	0(1)	3(1)	-1(1)
N(9)	16(1)	14(1)	16(1)	0(1)	3(1)	-1(1)
N(11)	16(1)	15(1)	18(1)	1(1)	4(1)	0(1)
N(12)	16(1)	14(1)	17(1)	0(1)	4(1)	-1(1)
N(13)	14(1)	15(1)	23(1)	-3(1)	3(1)	0(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3.

	x	y	z	U(eq)
H(2A)	4986	7923	4874	22
H(2B)	6683	7885	6208	22
H(3A)	8120	9775	4715	21
H(3B)	8584	9007	6114	21
H(4A)	4328	9081	2771	22
H(4B)	5586	9813	2707	22
H(13A)	-3082	5976	4853	21
H(13B)	-1807	5290	4508	21

Table S6. Hydrogen bonds for bt847 [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
N(2)-H(2A)...N(6)#1	0.88	2.11	2.9715(18)	165.0
N(2)-H(2B)...N(11)#2	0.88	2.12	2.8930(18)	146.3
N(3)-H(3A)...O(2)#3	0.88	2.14	3.0128(18)	168.7
N(3)-H(3B)...O(2)#2	0.88	2.57	3.2063(18)	130.3
N(3)-H(3B)...N(12)#2	0.88	2.59	3.3807(19)	149.2
N(4)-H(4A)...N(8)#1	0.88	2.10	2.9780(19)	173.7
N(4)-H(4B)...O(1)#3	0.88	1.99	2.8616(17)	171.0
N(13)-H(13A)...O(1)#4	0.88	2.29	3.1103(18)	156.1
N(13)-H(13B)...N(9)#5	0.88	2.21	3.0722(19)	168.3

Symmetry transformations used to generate equivalent atoms:

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

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

Computational details

Computations were performed with the Gaussian03 (Revision D.01) suite of programs.⁹

The geometric optimization of the structures based on single crystal structures, where available, and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,¹⁰ and single energy points 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.

The geometrical structures of the 3-amino-6-nitroamino-tetrazine anion have also been obtained by geometrical optimizations using density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) levels of theory and the NBO analysis¹¹ calculation was performed at the B3LYP/6-311+G(3df,2p) level.

Based on Born-Haber energy cycles, the heat of formation of an ionic salt can be simplified by the formula:

$$\Delta H_f^\circ(\text{ionic salt, 298K}) = \Delta H_f^\circ(\text{cation, 298K}) + \Delta H_f^\circ(\text{anion, 298 K}) - \Delta H_L$$

where ΔH_L is the lattice energy of the ionic salts which could be predicted by the formula suggested by Jenkins et al.¹² as:

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (\mathbf{A})$$

where n_M and n_X depend on the nature of the ions M_p^+ and Xq^- , respectively, and are equal to **3** for monatomic ions, **5** for linear polyatomic ions, and **6** for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (eq **B**) has the form

$$U_{\text{POT}}/\text{kJ mol}^{-1} = \gamma (\rho_m / M_m)^{1/3} + \delta \quad (\mathbf{B})$$

where density, $\rho_m/\text{g cm}^{-3}$, M_m is the chemical formula mass of the ionic material,

g (or Mg) and the coefficients $\gamma/\text{kJ mol}^{-1} \text{ cm}$ and $\delta/\text{kJ mol}^{-1}$) take the values from reference.¹²

Then the remaining task is to determine the heat of formation of the cation, which is computed using the method of isodesmic reactions.¹³ The enthalpy of reaction (ΔH_r°) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors. Thus, the heat of formation of the cation being investigated can be readily extracted.

With the value of the heats of formation and density of energetic salts, the expected detonation pressures (P) and detonation velocities (D) were calculated based on the traditional Chapman-Jouget thermodynamic detonation theory.¹⁴

Table S7 Cartesian coordinates of 3-amino-6-nitroamino-tetrazine anion (optimized from B3-LYP/6-31G(d,p) as input for NBO analysis) and charges distribution

Atom	Type	X	Y	Z	Mulliken charge	NBO charge
1	O	0.000000	0.000000	0.000000	-0.473914	-0.48912
2	O	0.000000	0.000000	2.183549	-0.507945	-0.48459
3	C	2.669111	0.000000	0.074153	1.376684	0.48224
4	C	4.118291	-0.317521	-2.045726	1.476365	0.47531
5	N	0.603325	0.060416	1.094142	0.340331	0.58927
6	N	1.935668	0.298044	1.170242	-0.518410	-0.44319
7	N	3.869966	0.658222	-0.004216	-0.581095	-0.24495
8	N	4.595089	0.495717	-1.093119	-0.575487	-0.29423
9	N	3.100832	-1.173971	-1.863874	-0.594990	-0.28490
10	N	2.367946	-1.032707	-0.780416	-0.547249	-0.23490
11	N	4.770956	-0.333680	-3.280943	-0.833555	-0.81756
12	H	4.668087	-1.230015	-3.741776	0.219437	0.37371
13	H	5.739196	-0.049036	-3.193679	0.219827	0.37291

Table S8 Total energy (E_0), zero-point energy (ZPE), values of thermal correction (H_T) of the compounds^a

Compound	ZPE	ΔH_T	E_0
NH ₂ NH ₂	140.2	11.0	-111.63188
NH ₃	90.3	10.0	-56.43462
CH ₃ NH ₂	168.1	11.5	-95.63188
CH ₄	117.6	10.0	-40.39849
CH ₃ NH(-) anion	132.3	11.0	-94.57290
3-amino-6-nitroamino tetrazine (-) anion	194.6	25.6	-609.85239
tetrazine	135.0	13.6	-295.72596
NH ₂ NO ₂	100.5	11.4	-260.55414
3-amino-6-nitroamino tetrazine	228.7	26.9	-610.37990
guanidine (+) cation	247.7	16.3	-205.33196
amino guanidine (+) cation	301.6	16.3	-260.54573
diamino guanidine (+) cation	350.8	18.7	-315.75835
triamino guanidine (+) cation	399.9	21.3	-370.97072
diguandinium tetrazine (+) cation	538.7	35.9	-703.95036

^a E_0 is in a.u.; ZPE and H_T are in kJ/mol. The scaling factors for the ZPE is 0.96.

Table S9 Heat of formation of small molecules used in the calculation

Compounds	NH ₂ NO ₂ ^a	Tetrazine ^a	Guanidine ^a	Guanidine cation ^a
HOE(kJ/mol)	-6.11	482.3	26.0	567.6
Compounds	CH ₄ ^b	NH ₃ ^b	CH ₃ NH ₂ ^b	NH ₂ NH ₂ ^b
HOE(kJ/mol)	-74.9	-45.9	-23.0	95.4

^a Calculated by G2 method;

^b Reference data.

References

- 1 D. E. Chavez and M. A. Hiskey, *J. Energ. Mater.* 1999, **17**, 357-377.
- 2 D. E. Chavez, M. A. Hiskey, and D. L. Naud, *Propellants, Explosives, Pyrotechnics* 2004, **29**, 209-215.
- 3 M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K. Y. Lee and D. G. Ott, *J. Heterocyclic Chem.* 1991, **28**, 2049-2050.
- 4 H. Hope, *Prog. Inorg. Chem.*, 1994, **41**, 1-19.
- 5 SMART: v.5.626, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, 2002.
- 6 SAINTPlus: v. 6.45a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2003.
- 7 SADABS: v.2.01, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, 2004.
- 8 SHELXTL: v. 6.10, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, 2001.
- 9 Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., 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.

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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, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

10 R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

11 (a) NBO Version 3.1, E.D. Glendening, A.E. Reed, J.E. Carpenter and F. Weinhold. (b) J. E. Carpenter and F. Weinhold, *J. Mol. Struct. (Theochem)* 1988, **169**, 41-62. (c) J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* 1980, **102**, 7211- 7218. (d) A. E. Reed, and F. Weinhold, *J. Chem. Phys.* 1983, **78**, 4066-4073. (e) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.* 1985, **83**, 735-746.

12 H. D. B. Jenkins, D. Tudeal, and L. Glasser, *Inorg. Chem.* 2002, **41** , 2364-2367.

13 M. W. Schmidt , M. S. Gordon and J. A. Boatz, *J. Phys. Chem., A*, 2005, **109**, 7285-7295.

14 L.E. Fried, K.R. Glaesemann, W.M. Howard, and P.C. Souers, 2004. *CHEETAH 4.0 User's Manual.*, Lawrence Livermore National Laboratory.