Computational insight into a new family of functionalized tetrazole-N-oxides as high-energy density materials

Piao He[1]*, Jingjie Han[1], Jinting Wu[2], Haozheng Mei[3], Jianguo Zhang[3]

Table of Contents

1. Optimized parameters

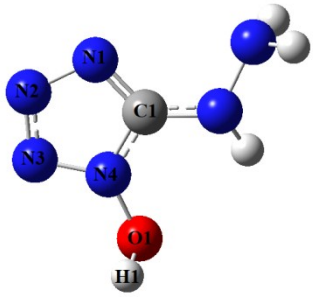

Figure S1 Optimized geometry of compound **1**

Table S1 Selected optimized parameters of tetrazole N-oxides **1-10**

Bond length/angles[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C1-N1	1.317	1.358	1.416	1.349	1.325	1.352	1.339	1.322	1.322	1.315
N1-N2	1.370	1.364	1.440	1.357	1.349	1.347	1.298	1.357	1.366	1.371
N2-N3	1.282	1.266	1.450	1.281	1.303	1.273	1.324	1.288	1.279	1.281
N3-N4	1.358	1.355	1.429	1.367	1.327	1.349	1.312	1.345	1.360	1.359
N4-C1	1.354	1.372	1.287	1.320	1.348	1.354	1.344	1.343	1.345	1.348
N-O	1.370	1.354	1.451	1.364	1.362	1.341	1.352	1.362	1.363	1.365
N1-N2-N3	112.4	108.2	106.5	105.4	111.2	107.9	116.4	110.7	111.5	112.0
N2-N3-N4	104.7	107.3	106.4	111.7	105.6	107.3	104.7	105.5	105.4	105.2

*Corresponding authors: Piao He, E-mail: piaohe@csu.edu.cn

O-N-C1(N)	126.0	126.0	104.1	125.9	129.8	128.8	122.7	126.7	125.9	126.4
H-O-N	105.6	106.3	102.5	105.9	105.0	102.1	104.3	105.7	105.9	105.8
N1-N2-N3-N4	2.2	0.8	13.3	2.1	0.0	1.7	0.0	1.3	1.6	2.1
O-N-N-N	170.9	169.0	97.5	172.1	179.3	172.5	179.7	175.7	173.4	172.1
N-N-O-H	76.1	115.6	110.0	70.5	176.0	145.8	1.2	58.8	66.9	80.8

a Bond length (Å), Bond angle (º), Dihedral angle (º).

Cartesian coordinates of optimized geometry

Compound **1**

SCF energy = -444.2148905 hartree

ZPE = 0.083869 hartree

Atom	X	Y	Z
N	-1.32366900	-1.53574300	0.01556700
N	1.48593700	0.53675400	-0.12046300
C	0.29660900	-0.13585800	-0.04841600
N	0.04183000	-1.42884400	-0.02952700
N	-1.90419100	-0.39230400	0.04042800
H	1.46011300	1.48250900	0.24458700
N	-0.89317000	0.51176400	-0.04151100
O	-1.07655500	1.85834800	0.13345100
H	-1.48513400	2.17571700	-0.68617400
N	2.66249800	-0.21222500	0.03436600
H	3.36298400	0.12027100	-0.61541800
H	3.01018100	-0.18595800	0.98787400

Compound **2**

SCF energy = -593.4187764 hartree

ZPE = 0.069315 hartree

Atom	X	Y	Z

N	1.85686200	1.51579900	-0.00637200
N	-0.85273800	-0.78241800	-0.01156000
C	0.22075500	-0.03187400	-0.00341600
N	0.50984500	1.29514000	-0.00362000
H	-0.17633900	2.03790800	0.02186900
N	2.44335300	0.39301500	-0.02234400
N	1.48464700	-0.56414800	-0.05031900
O	1.81023900	-1.86344000	0.14905700
H	1.60945900	-2.32547700	-0.68066600
N	-2.05713200	-0.09054700	0.00248300
O	-3.05617200	-0.77738300	-0.02241900
O	-2.06050600	1.15468700	0.03853900

Compound **3**

SCF energy = -445.4244743 hartree

ZPE = 0.107552 hartree

Atom	X	Y	Z
N	1.98223700	-1.15351500	0.10428700
H	1.99286600	-2.01774000	0.62516900
C	0.74750800	-0.63738900	-0.14140800
N	0.63759700	0.74096200	-0.45087500
H	2.67608100	-0.47280300	0.37829300
N	-0.35402100	-1.30310000	-0.18136300
N	1.14019900	1.56917200	0.58545200
H	1.33033200	2.48115600	0.18668200
H	0.43715100	1.67296500	1.31760400
N	-1.40170300	-0.35726400	-0.40530000
N	-0.75841000	0.88945400	-0.77337000
H	-0.80929100	0.89412200	-1.78952300
O	-1.98751300	-0.15938300	0.90759800

H	-2.93337700	-0.15824900	0.71762100

Compound **4**

SCF energy = -742. 2997777 hartree

ZPE = 0.108703 hartree

Atom	X	Y	Z
N	3.14685000	-1.38468400	0.01787700
N	0.22354200	0.51680600	-0.00476800
H	0.15373300	1.52577000	0.03803600
C	1.45799400	-0.05897600	-0.00294700
N	1.78040100	-1.33900300	0.01749400
N	3.66164100	-0.21135200	0.01359200
N	2.60916200	0.64416900	-0.03772500
O	2.72595700	1.99697600	0.09734300
H	3.16160700	2.30971000	-0.71146800
C	-1.00296300	-0.14350300	-0.00681700
N	-1.00117200	-1.47186900	-0.01793300
H	-0.12223700	-1.98243000	-0.00537500
H	-1.91166400	-1.91731900	-0.02166500
N	-2.00055900	0.72695100	-0.00045300
N	-3.30075100	0.25368300	0.00242200
O	-4.16042800	1.11261900	0.02248700
O	-3.54620600	-0.96756500	-0.01664000

Compound **5**

SCF energy = -649.8139332 hartree

ZPE = 0.092732 hartree

Atom	X	Y	Z
N	-2.88829700	-0.14552800	0.01623200
N	-1.01324100	-1.41215700	0.02325500

C	-0.66419800	-0.15416000	-0.00575700
N	1.76913000	-0.58743100	-0.01154200
N	2.89995800	0.10839500	0.01192900
N	2.54229600	1.36120300	0.03566000
N	1.19876500	1.48663300	0.02819600
C	0.71446400	0.25353900	-0.00525500
O	1.79883700	-1.94916500	-0.05327400
H	0.85920500	-2.22540600	0.00097400
C	-1.85081100	0.65834500	-0.01345900
O	-2.36580800	-1.43444900	0.03550500
N	-1.89590700	2.00995500	-0.08370400
H	-1.03780900	2.52219800	0.06309700
H	-2.77128500	2.47828100	0.08472500

Compound **6**

SCF energy = -781.9333488 hartree

ZPE = 0.083301 hartree

Atom	X	Y	Z
C	-0.74244300	0.03579400	-0.02087900
N	1.69922600	-0.54946600	-0.22507700
N	2.88575800	0.07235400	-0.05790300
N	2.64064200	1.27949000	0.26655700
C	0.65761000	0.27727300	0.03482700
O	1.68151600	-1.79722500	-0.71708800
H	0.89702300	-2.20795300	-0.22923900
N	-1.61998700	1.16454000	-0.16991900
O	-1.10559100	2.28069600	0.05798000
O	-2.77404800	1.01078900	-0.51019600
N	-1.27047700	-1.24937300	0.23617200
O	-2.45920700	-1.47680100	0.18720300

O	-0.43013600	-2.13848200	0.58707800
N	1.30373700	1.42387600	0.34648100
H	0.83942100	2.30779700	0.53156000

Compound **7**

SCF energy = -986.4594769 hartree

ZPE = 0.083793 hartree

Atom	X	Y	Z
N	-1.66455200	-0.77560300	-0.02321800
N	-2.65161900	1.22310500	-0.07940600
C	-0.77840100	0.22843400	-0.06210600
N	-1.35700900	1.44131600	-0.08960400
N	-2.77056500	-0.09522000	-0.03923300
O	-3.96861000	-0.72173800	-0.02112400
H	-4.61872900	0.00197600	-0.02404600
C	0.68555700	-0.00533500	-0.00864900
N	1.45683100	1.33240400	0.14646400
O	2.06140700	1.50718300	1.17800900
O	1.36608000	2.06364300	-0.81083700
N	1.04357700	-0.92444800	1.20924400
O	0.44426500	-0.66066600	2.22528300
O	1.87313300	-1.78317200	1.02558000
N	1.27611600	-0.69887400	-1.28276300
O	0.50946100	-1.40048700	-1.90143700
O	2.44505400	-0.48718100	-1.50069800

Compound **8**

SCF energy = -705.1534016 hartree

ZPE = 0.110010 hartree

Atom	X	Y	Z

N	-0.99148200	1.22469400	-0.07362500
N	-2.19145300	1.60124100	-0.58455400
N	-3.02540100	0.61942400	-0.55995600
N	2.07637500	-1.51571100	-0.37889700
N	3.18072800	-0.83052200	-0.77978500
N	3.10976400	0.41597500	-0.43627100
C	-1.08801900	-0.05052100	0.26144700
C	-0.02070400	-0.90351500	0.86958200
H	-0.25896000	-1.95828100	0.73193000
H	0.01323400	-0.71025800	1.94821900
C	1.31641100	-0.64657300	0.25355300
N	1.94859900	0.54532500	0.21240600
N	-2.34080600	-0.42137100	-0.05081600
O	1.57600800	1.72849600	0.77283100
H	0.68694800	1.91468400	0.37802000
O	-2.92242200	-1.62630800	0.20673900
H	-3.28029900	-1.93338500	-0.64172600

Compound **9**

SCF energy = -721.1912969 hartree

ZPE = 0.098294 hartree

Atom	X	Y	Z
N	-0.02046700	-0.92412100	-0.36456600
H	-0.21914400	-1.91260700	-0.45252700
N	-3.11672500	0.62052900	0.29795500
N	-2.29216300	1.57780200	0.49885400
N	-1.00068200	1.17788100	0.30067600
N	2.20144200	-1.47284800	0.36160900
N	3.35562800	-0.76181600	0.47453300
N	3.18359300	0.47585200	0.14828400

C	-1.05331400	-0.10057400	-0.03195700
C	1.30665900	-0.61972900	-0.08202400
N	1.89514500	0.58499300	-0.21805700
N	-2.34973900	-0.46093000	-0.00765700
O	1.41606800	1.73792400	-0.75604800
H	0.56574600	1.90396800	-0.27091300
O	-2.85637700	-1.65930300	-0.41649300
H	-3.33643000	-2.01991100	0.34623700

Compound **10**

SCF energy = -776.5196799 hartree

ZPE = 0.114408 hartree

Atom	X	Y	Z
N	-2.80529100	-0.31888100	0.02042600
N	-3.46580300	0.60382700	0.76873100
N	-2.60875800	1.52873300	0.99639600
N	-1.40708100	1.27910200	0.38398300
C	-1.55725200	0.12668800	-0.23178300
N	2.74480500	0.35760600	-0.12711400
N	3.51535800	-0.25024800	0.80960600
N	2.84407300	-1.28140800	1.17426200
N	1.63267400	-1.36004400	0.54000000
C	1.58573100	-0.31805400	-0.25914700
N	0.61045600	0.04136800	-1.17199000
H	0.56508100	1.04080800	-1.35429900
N	-0.63136500	-0.55419800	-0.97488800
H	-0.95848700	-1.11858400	-1.74597300
O	3.03355300	1.58255100	-0.66152100
H	3.79619000	1.44236600	-1.24379200
O	-3.41722500	-1.39251400	-0.56160700

H -3.50774300 -2.05768000 0.13879200

2. HOMO-LUMO and energy gap

Table S2 HOMO-LUMO and energy gap of tetrazole N-oxides **1-10** (eV)

Energy	LUMO	HOMO	$\Delta E_{LUMO-HOMO}$
1	-1.11	-7.14	6.02
2	-2.56	-8.02	5.46
3	-0.50	-6.45	5.95
4	-2.49	-7.97	5.47
5	-2.89	-7.67	4.77
6	-3.48	-8.13	4.64
7	-3.89	-9.23	5.34
8	-1.99	-8.19	6.20
9	-1.85	-7.87	6.01
10	-1.23	-7.68	6.45

3. Thermodynamic parameters

Table S3 Thermodynamic parameters of tetrazole N-oxides **1-10**

Energy	ZPE (kcal/mol)	*U* (kcal/mol)	*H* (kcal/mol)	*G* (kcal/mol)	*S* (kcal/(mol·K))	C_v (kcal/(mol·K))
1	52.62	57.31	57.91	32.62	84.79	26.34
2	43.49	48.69	49.28	22.16	90.97	28.92
3	67.48	72.32	72.91	47.60	84.88	29.30
4	68.21	75.31	75.90	43.72	107.91	40.57
5	58.19	64.28	64.87	35.80	97.51	35.77
6	52.27	58.66	59.25	28.96	101.58	36.94
7	52.58	61.37	61.961	25.61	121.91	47.65
8	69.03	75.51	76.10	45.72	101.88	37.69
9	61.68	68.09	68.68	38.70	100.57	37.7
10	71.79	79.39	79.98	46.48	112.37	43.34

4. Calculations description

Density is one of the important parameters for an energetic material. The density was predicted by using an improved equation proposed by Politzer[1] referring to intermolecular interactions within the crystal as follows:

$$\rho = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\left(\upsilon\sigma_{Tot}^2\right) + \gamma \quad (1)$$

Where M is molecular mass in g/molecule; V(0.001) is volume in cm^3/molecule, which is average value of calculated molecular volumes by using a Monte Carlo integration embedded in Gaussian program[2]; The $\upsilon\sigma^2_{Tot}$ is derived from the molecular electrostatic potential calculation, which is performed by using Multiwfn program[3]; α, β and γ are coefficients from the reference[1].

The heat of formation is often used to evaluate the energy performance of energetic compounds. Here we give the atomization energies method[4] to calculate the heat of formation of gas-phase:

$$\Delta H_f\left(A_xB_y, 0K\right) = x\Delta H^0(A, 0K) + y\Delta H^0(B, 0K) - \sum D_0 \quad (2)$$

Where ΔH^0 is the heat of formation of isolated atoms; D_0 is calculated atomization energies.

Then, the heat of formation was determined by deducting the enthalpy of sublimation either vaporization[5, 6] based on the Hess' law[7].

$$\Delta H(Solid) = \Delta H(Gas) - \Delta H(Sublimation) \quad (3)$$

$$\Delta H(Liquid) = \Delta H(Gas) - \Delta H(Vaporization) \quad (4)$$

$$\Delta H(Subimation) = a(SA)^2 + b\sqrt{\sigma_{Tot}^2\upsilon} + c \quad (5)$$

$$\Delta H(Vaporization) = a\sqrt{(SA)} + b\sqrt{\sigma_{Tot}^2\upsilon} + c \quad (6)$$

Where (SA) is the molecular surface area for this structure, σ^2_{Tot} is described as an indicator of the variability of the electrostatic potential on the molecular surface, and υ is the degree of balance between the positive and negative potentials on the molecular surface. And where a, b, and c are fitting parameters.

Table S4 The detailed parameters for calculating the heats of formation of tetrazole N-oxides **1-10**

	[a] E	[b] ZPE	[c] H_{corr}	[d] SA	[e] σ^2_{Tot}	[f] υ	[g] ΔH_{0K}	[h] ΔH_{298K}	[i] $\Delta H_{(Subimation)}$	[j] $\Delta_f H_{298K(s)}$
1	-444.2148	0.0838	0.0922	139.0491	405.1134	0.2458	130.9563	124.6687	27.1964	97.4722
2	-593.4187	0.0693	0.0785	149.6185	385.6064	0.1897	121.1890	115.3509	24.8084	90.5425
3	-445.4244	0.1075	0.1161	142.8043	230.6029	0.2493	120.2681	112.1036	21.4625	90.6411
4	-742. 2997	0.1087	0.1209	190.9808	397.0834	0.1916	133.0656	124.7770	31.2132	93.5637
5	-649.8139	0.0927	0.1033	171.8645	205.2510	0.2064	163.1335	156.6771	21.9519	134.7251
6	-781.9333	0.0833	0.0944	173.1789	264.2107	0.1839	121.5714	114.5975	23.9454	90.6521
7	-986.4594	0.0837	0.0987	203.6436	320.2922	0.0528	148.4166	141.7303	21.4434	120.2869
8	-705.1534	0.1100	0.1212	187.9477	384.4316	0.1948	190.3370	182.2184	30.5493	151.6691
9	-721.1912	0.0982	0.1094	183.1384	458.0306	0.1575	201.3868	193.4236	29.3825	164.0410
10	-776.5196	0.1144	0.1274	205.1156	415.0451	0.1809	234.8165	225.9912	33.4316	192.5596

[a] E is electronic energies (hartree), [b] ZPE is zero-point correction (hartree), [c] H_{corr} is thermal correction to enthalpy (hartree), [d] SA is the molecular surface area for this structure (Å^2), [e] σ^2_{Tot} is an indicator of the variability of the electrostatic potential ((kcal/mol)^2), [f] υ is the degree of balance, [g] ΔH_{0K} is heats of formation for gas at 0K (kcal/mol), [h] ΔH_{298K} is heats of formation for gas at 298K (kcal/mol), [i] $\Delta H_{(Subimation)}$ is the enthalpy of sublimation (kcal/mol), [j] $\Delta_f H_{298K(s)}$ is the heat of formation for solid at 298K (kcal/mol).

The detonation velocity and detonation pressure are the key parameters to assess the potential of an energetic material and were predicted by Empirical Kamlet-Jacobs equations[8]:

$$V_D = 1.01\left(N\bar{M}^{\frac{1}{2}}Q^{\frac{1}{2}}\right)^{\frac{1}{2}}(1 + 1.30\rho) \quad (7)$$

$$P_D = 1.558\rho^2 N\bar{M}^{\frac{1}{2}}Q^{\frac{1}{2}} \quad (8)$$

Where V_D is detonation velocity (km/s); P_D is detonation pressure (GPa); N is moles of detonation gases per gram explosive; $\bar{M}$ is average molecular weight of these gases; Q is heat of detonation (cal/g); and ρ is the theoretical density (g/cm^3) here.

In order to investigate the sensitivity of explosives, the property-structure relation method "generalized interaction property function" (GIPF)[9] was used to estimate the impact sensitivity $h_{50\%}$. Here we give introduced Model 4 summarized below:

Model 4: $h_{50\%} = 27.8 + 0.1135 \times \exp[-(2.6479\ \text{g/kJ} \times [Q_d - 6.9496\ \text{kJ/g}])]$ (9)

Table S5 The calculated $h_{50\%}$ based on the model 4 of tetrazole N-oxides **1-10** common HEDMs

$h_{50\%}$	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**TNT**	**RDX**	**HMX**
Model 4	28	28	29	28	28	29	28	28	28	28	113	39	41
Exp.	--	--	--	--	--	--	--	--	--	--	98	28	32

5. References

1. P. Politzer, J. Martinez, J. S. Murray, M. C. Concha and A. Toro-Labbé, *Mol. Phys.*, 2009, **107**, 2095-2101.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *GAUSSIAN 09*, (2009) Gaussian, Inc., Wallingford CT.
3. T. Lu, *Multiwfn, version 1.4:* http://multiwfn.codeplex.com/.
4. L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.*, 1997, **106**, 1063-1066.
5. J. S. Murray and P. Politzer, *Quantitative Treatment of Solute/Solvent Interactions, Theoretical and Computational Chemistry*, Elsevier Scientific, Amsterdam, 1994.
6. P. Politzer, J. S. Murray, T. Brinck and P. Lane, *Immunoanalysis of Agrochemicals*, ACS Symp. Ser. 586, American Chemical Society, Washington, DC, 1994.
7. P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1982.
8. M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48**, 23-35.
9. B. M. Rice and J. J. Hare, *J. Phys. Chem. A*, 2002, **106**, 1770-1783.