

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

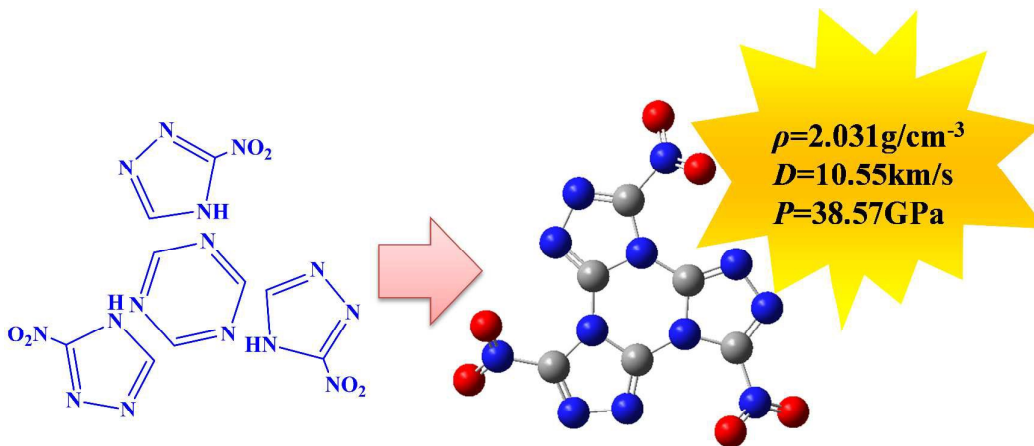
You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

**Theoretical studies on the derivatives of
tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine as high
energetic compounds**

Qun Zeng, Yanyang Qu, Jinshan Li and Hui Huang*

*Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, 621900,
China*



Tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine inherited from triazole and triazine is suggested theoretically as a new framework for insensitive and high-energetic materials.

* Corresponding Author
E-mail: huangh0816@sina.com

Abstract: A heterocyclic framework inherited from triazole and triazine was suggested for the design of new energetic compounds. The geometric and electronic structures, IR spectra, gas and condensed-phase heat of formation of tris ([1,2,4] triazolo)[4,3-a:4',3'-c:4'',3'''-e][1,3,5]triazine (TTT) and its nitro, amino, nitramino, and azide functionalized derivatives have been studied with *ab initio* and density functional theory methods. The crystal structures of these compounds were predicted using the crystal packing model. The initial decomposition reactions in gas phase were studied to examine their kinetic stability. Our calculated results indicate that these compounds are promising candidates for energetic materials. In particular, 3,7,11-trinitrotris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3'''-e][1,3,5]triazine (TNTTT) has a density of 2.031 g/cm³, heat of formation of 208.37 kcal/mol, detonation velocity of 10.55 km/s, pressure of 38.57 GPa, and high activation energy of 55.97 kcal/mol, which are in general better than the commonly used energetic materials.

Keywords: Density functional theory (DFT);

Tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3'''-e][1,3,5]triazine (TTT) ; Enthalpy of formation;

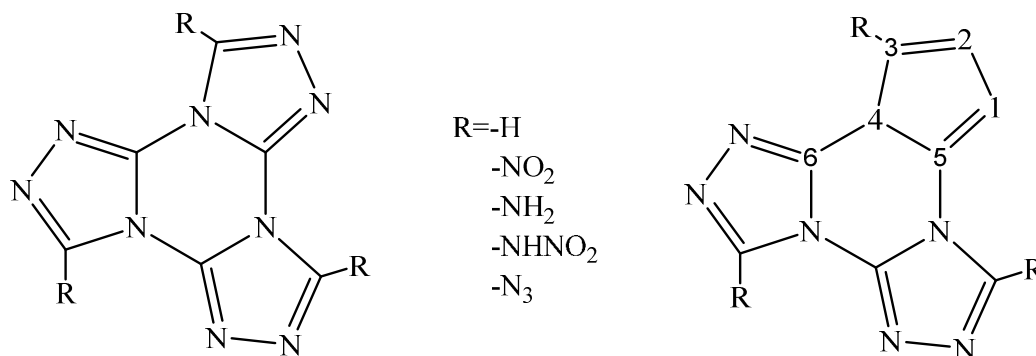
Electronic structure; Stability; Detonation performance

Introduction

Energetic materials are widely used in modern civil and military applications.¹⁻⁴ In order to meet a variety of requirements in reactivity, safety and environment, much effort has been taken to the design and synthesis of new energetic materials referring to novel performances,⁵⁻⁷ especially for the materials with great power and high safety. However, in most cases, it is very difficult to concentrate both desired properties into one compound. As one kind of interesting structures, high-nitrogen heterocyclic systems have attracted great attention for the development of high-energy compounds.⁸⁻¹⁴ Because nitro and some other energetic groups are presented on the rings, this type of compounds could be used as high performance explosives.¹⁵⁻¹⁸ Moreover, nitrogen-containing aromatic heterocycles are insensitive because of their aromaticity.^{1, 18, 19} Among these heterocycles, 1, 2, 4-triazole and triazine groups with good stability, high nitrogen content, high enthalpy of formation, etc. are efficient fragments to enhance the performance of high-energy compounds.²⁰⁻²⁴ It is thus expected that a new backbone combining with 1, 2, 4-triazole and 1, 3, 5-triazine fragments would derive new energetic molecules with good performances both in power and insensitivity.

Tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine (TTT) is one of the frameworks containing 1, 2, 4-triazole and 1, 3, 5-triazine. As shown in Scheme 1, three triazole units are fused into one triazine ring to form a large planar conjugated structure with high nitrogen content.²⁵ Although the framework inherited from triazole and triazine has good potential for high power and low sensitivity, as far as we know, no attention has been paid to this framework for energetic materials purpose. In this work the detonation and stability of TTT and several functionalized derivatives have been studied to examine our expectation by means of *ab initio*, density functional theory (DFT) and molecular mechanics methods. The crystal structures, electronic structures, heats of formation (HOFs), initial decomposition reactions, detonation velocities and pressures have been investigated to understand the energetics and stability of these compounds. Our study would be helpful for the

experimental research about the energetic compounds with TTT framework and other nitrogen-enriched conjugated structures.

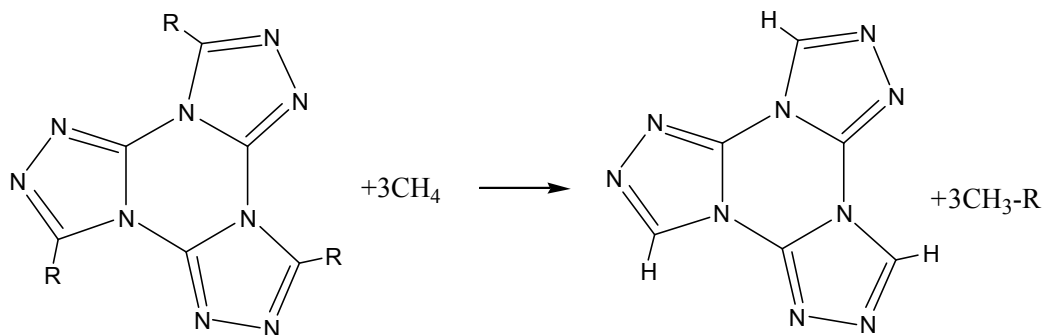


Scheme 1 The structures and atomic numbering of tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine (TTT), four functionalized derivatives.

Computational methods

In this theoretical work, all *ab initio* and DFT calculations were performed with Gaussian 09 package.²⁶ For these heterocyclic compounds, geometry optimization of the molecular structures was carried out at the M06-2X/cc-pVTZ level.^{27, 28} The harmonic frequency calculations were performed at the same level in order to ensure that the structures are local minima on the potential energy surfaces. Molecular electrostatic potentials (MEPs) were obtained at the same level. Finally, the possible initial decomposition reactions were studied with M06-2X/cc-pVTZ to understand the stability referring to chemical processes directly, and all geometries of transition states were confirmed with their intrinsic reaction coordinates (IRC).

In order to get the standard gas-phase HOFs ($\Delta_f H_{\text{gas}}^\circ$) at 298 K, a series of isodesmic reactions²⁹ were designed to obtain HOFs as shown as follows:



Scheme 2 Designed isodesmic reactions for four TTT derivatives.

For each isodesmic reaction, the $\Delta_f H_{\text{gas}, 298\text{K}}^\circ$ is calculated by the following equation:

$$\Delta_f H_{\text{gas}, 298\text{K}}^\circ = \sum \Delta_f H_{\text{P}} - \sum \Delta_f H_{\text{R}} = \Delta E_0 - \Delta \text{ZPE} + \Delta H_{\text{T}} + \Delta nRT \quad (1)$$

where $\Delta_f H_{\text{P}}$ and $\Delta_f H_{\text{R}}$ are the HOFs of products and reactants at 298 K, respectively. ΔE_0 is the difference between the electron energies of products and reactants at 0 K. ΔZPE is the difference between the zero-point energies (ZPEs) of products and reactants, and ΔH_{T} is the thermal correction from 0 K to 298 K. ΔnRT is the work term, which is equal to zero because Δn is zero in Scheme 2. Since no measured values are available for the reference molecules, additional calculations were performed for their atomization reactions at the G3B3 level.³⁰ Further single point calculations for the M06-2X/cc-pVTZ optimized structures were performed with a larger aug-cc-pVTZ³¹ basis set.

Based on Hess's law,³² the condensed-phase HOFs ($\Delta_f H_{\text{Cond}}^\circ$) were obtained by

$$\Delta_f H_{\text{Cond}}^\circ = \Delta_f H_{\text{gas}}^\circ - \Delta H_{\text{sub}} \quad (2)$$

where ΔH_{sub} is the heat of sublimation and can be evaluated by the Byrd and Rice method³³ in the framework of the Politzer approach.³⁴

$$\Delta H_{\text{sub}} = \alpha_1 A^2 + \alpha_2 (v\sigma_{\text{tot}}^2)^{0.5} + \alpha_3 \quad (3)$$

Meanwhile, the density of energetic crystal was estimated with a similar empirical expression:^{35, 36}

$$\rho = \beta_1 \left(\frac{M}{V} \right) + \beta_2 (v\sigma_{tot}^2) + \beta_3 \quad (4)$$

In these expressions, A and V are the area of isosurface of 0.001 electrons/bohr³, and the volume contained within such isosurface respectively. v is the degree of balance between the positive and the negative potential on the molecular surface. σ_{tot}^2 is the measure of variability of the electrostatic potential. M is the molecular weight of compound. α_i , and β_i ($i = 1, 2, 3$) are empirical parameters that are fitted from experiment measures.^{33, 36} All of these parameters about surface were obtained in Multiwfn program³⁷ at the M06-2X/cc-pVTZ level. Combined with density and $\Delta_f H_{\text{Cond}}^\circ$, the detonation velocities (D) and pressures (P) of these compounds were predicted with Explo5 (version 6.02) package which is based on the chemical equilibrium, steady-state model detonation.³⁸ The equilibrium composition of the detonation products can be estimated by the modified White, Johnson, and Dantzig's free energy minimization technique, combining with the Becker–Kistiakowsky–Wilson equation of state (BKW-EOS), which is used for gaseous detonation products and the Cowan–Fickett equation of state for solid carbon. The program is designed for predicting the detonation properties at the CJ point.

Because the energetic compounds are usually in solid, the possible polymorphs and crystal structure of the compounds were predicted by Dreiding force field and polymorph module of Materials Studio.³⁹ Because more than 80% organic compounds are crystallized in seven space groups ($P2_1/c$, $P\bar{1}$, $P2_12_12_1$, $Pbca$, $C2/c$, $P2_1$ and $Pna2_1$) according to the statistical data,^{40,41} the crystal prediction has been constrained to these most typical groups. The geometries which are optimized at the M06-2X/cc-pVTZ level were used for the polymorph search.

Results and discussion

Molecular Geometry

In order to explore the TTT framework, nitro, amino, nitramino, and azide

nitrogen-containing groups have been chosen to replace the hydrogen atoms in the derivatives shown in Scheme 1. These compounds should be obtained according to the syntheses of several known TTT's derivatives in the viewpoint of organic chemistry.^{25, 42, 43} It is evident that three five-membered rings and one six-membered ring construct a framework with a C_3 axis for all compounds.

Table 1 The bond-lengths of TTT and its derivatives (in Å)

Bond	TTT	R=NO ₂	R=NH ₂	R=NHNO ₂	R=N ₃
N1–N2	1.381	1.372	1.394	1.375	1.382
N2=C3	1.295	1.285	1.302	1.295	1.298
C3–N4	1.376	1.375	1.378	1.376	1.379
N4–C5	1.369	1.376	1.375	1.370	1.379
C5=N1	1.288	1.289	1.281	1.289	1.285
N4–N6	1.385	1.390	1.384	1.385	1.388
C3–R	1.076	1.461	1.357	1.385	1.379

Table 1 lists the selected bond lengths of the optimized structures. TTT exhibits a standard planar structure with C_{3h} symmetry. Three types of bonds, N–N, C=N, and C–N, exist in the framework. These bondlengths have very small changes when the H atoms are substituted. Take N4–C6 bond as an example, its length is about 1.385 Å in TTT, **2**, and **3** and becomes 1.390 Å in **1**. Although inheriting from the planar TTT, the frameworks in **1**, **2**, and **3** do not retain their perfect planes due to the steric effect of substituent groups. Moreover, most atoms in the nitro, amino, and nitramino groups are not located on the planes of the frameworks. In the four derivatives, all C3-R bonds are C-N single bonds with bond lengths of 1.461, 1.357, 1.385, and 1.379 Å, respectively. Overall, most of these compounds possess the compact symmetric structures.

Crystal structure and Density

The predicted lattice parameters of five compounds are presented in Table 2. All compounds are among three space groups, namely, $P2_1/c$, $Pna2_1$, and $Pbca$, according to their energy orders. Fig. 1 shows the cell structures of compound **1** and **3**. Eight

molecules of compound **1** and four molecules of compound **3** respectively construct two orthogonal cells with *Pbca* and *Pna2₁* symmetries. And the predicted cell structures of compound TTT, **2** and **4** are presented in Fig. S1.

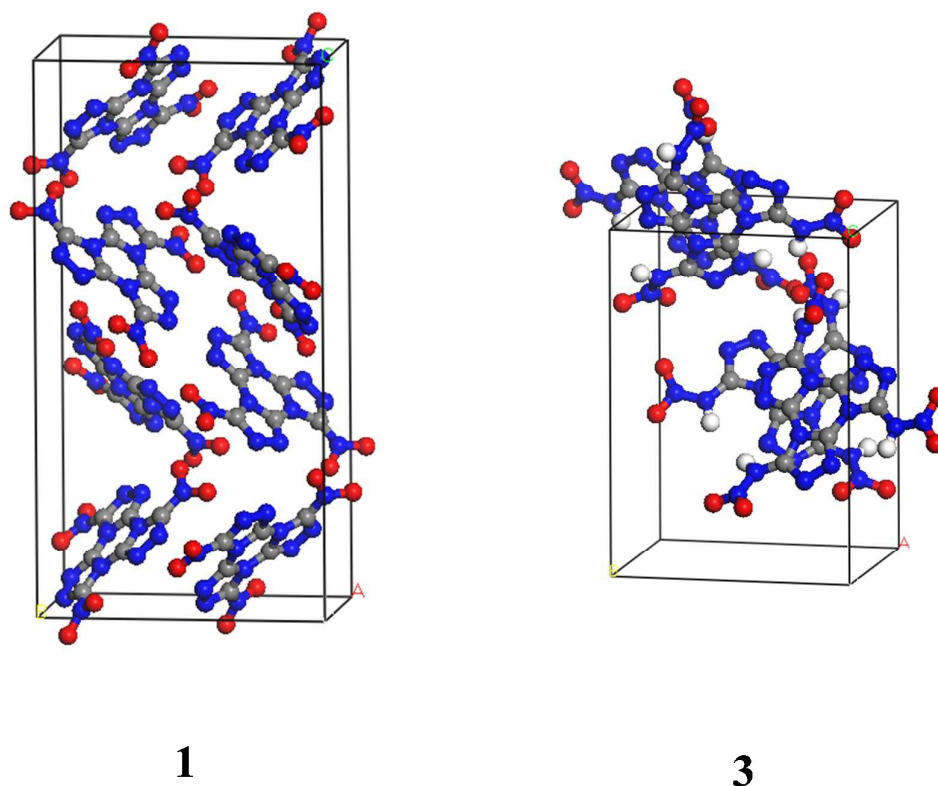


Fig.1 The cell structures of compound **1** and **3**.

Density is one of the most attractive properties in energetic materials. Based on the cell structure, the crystal densities were estimated for these compounds, as listed in Table 2. Obviously, these TTT framework-containing compounds have high densities. The density of **1** with nitro-groups is as high as 2.031 g/cm³, close to 2.035 g/cm³, the density of ϵ -CL-20 (2,4,6,8,10,12-hexanitrohexaazaisowurtzitane). The density of **3** with nitramino-groups is 1.905 g/cm³, higher than those of β -HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane, 1.903 g/cm³) and BTF (benzotrifuroxan, 1.901 g/cm³). For **2** and **4**, the predicted densities are 1.824 and 1.792 g/cm³, respectively. At the same time, another series of density (ρ') were obtained by using Eq. 4, which are lower than those above, as shown in Table 3. For example, the predicted densities

of **1** and **3** are 1.904 and 1.866 g/cm³, respectively. In short, compound **1** and **3** are expected to possess high densities, which is one of the indicators of good detonation performances.⁴⁴

Table 2 The cell parameters of possible molecular packings

Compound	Space groups	Z	ρ (g/cm ³)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
TTT	<i>P2₁/c</i>	4	1.728	9.081	14.159	14.159	90.00	61.28	90.00
1	<i>Pbca</i>	8	2.031	7.577	12.237	23.716	90.00	90.00	90.00
2	<i>Pna2₁</i>	4	1.824	7.209	15.449	8.047	90.00	90.00	90.00
3	<i>Pna2₁</i>	4	1.905	9.069	10.089	14.528	90.00	90.00	90.00
4	<i>P2₁/c</i>	4	1.792	10.501	13.127	16.785	90.00	31.28	90.00

Table 3 The calculated densities from Eq. 4, heat of sublimation and formation, energy gaps, net charge on R group, and oxygen balance of the compounds

Compound	ρ' (g/cm ³)	$\Delta_f H_{\text{gas}}$ (kcal/mol)	ΔH_{sub} (kcal/mol)	$\Delta_f H_{\text{cond}}$ (kcal/mol)	E_{gap} (eV)	$Q(\text{R})$ (e)	OB (%)
TTT	1.675	192.69	23.64	169.32	8.83	0.198	-59.7
1	1.904	176.45	29.41	208.37	7.91	-0.080	0.0
2	1.696	237.78	29.15	130.44	8.25	0.064	-58.5
3	1.866	245.18	37.36	207.82	8.26	-0.028	-6.3
4	1.803	439.07	36.68	402.40	7.74	0.047	-29.6

Vibration Analysis and Heats of Formation

Infrared (IR) spectrum is often employed to identify the structures of substances and closely related to their thermodynamics properties. The simulated IR spectra of TTT and its derivatives are shown in Fig. 2. For the TTT framework, only one strong characteristic peak was characterized at 1683 cm⁻¹ corresponding to the asymmetrical stretching of N–C in the six-membered ring. When the hydrogen atoms are substituted by the functional groups, the peaks in compound **1**, **3** and **4** remain around 1650 cm⁻¹, except the peak at 1729 cm⁻¹ in **2**. Some additional peaks belonging to the substituent groups appear in the IR spectra. In compound **1**, the strongest peak at 1743 cm⁻¹ is associated with the asymmetrical stretching vibrations of N–O bonds in the nitro groups, while the medium peaks at 1457 cm⁻¹ are mainly dominated by the stretching vibration of C–NO₂ bonds. In compound **2**, the strongest peak at 1668 cm⁻¹ is assigned to the stretching of C–NH₂ bonds. The asymmetrical and symmetrical stretching

modes of N–H bonds correspond to two medium peaks at 3565 and 3706 cm^{-1} , and the out-of-plane vibrations refer to the weak peak at 475 cm^{-1} . For compound **3**, the strongest peaks are observed at 1770 cm^{-1} referring to the stretching vibrations of N–NO₂ bonds. The three medium peaks at 1380, 1394 and 1430 cm^{-1} respectively belong to the stretching of –C–NH–, the rocking modes of N–H, and the stretching of N–O. The out-of-plane and stretching modes of N–H refer to the weak peaks at 520 and 3581 cm^{-1} . For compound **4**, the strongest peak at 2381 cm^{-1} is assigned to the stretching vibration of =N=N= bonds, and the stretching modes of –N=N= and C–N= refer to the medium peaks at 1291 and 1599 cm^{-1} .

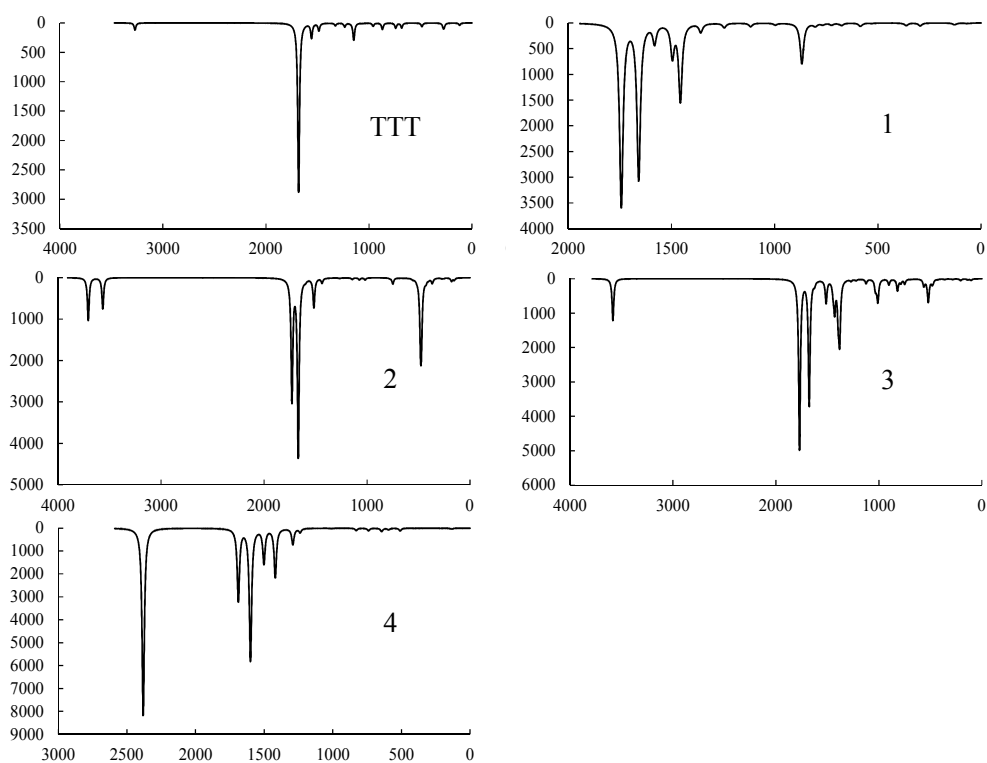


Fig. 2 The M06-2X/cc-pVTZ simulated IR spectra of TTT and its derivatives.

Based on the vibrational analysis and statistic thermodynamic methods, the gaseous-phase HOFs of the compounds were estimated and tabulated in Table 3. Using atomization reaction at G3B3 level, HOF of TTT were predicted as high as 192.69 kcal/mol. $\Delta_f H_{\text{gas}}^\circ$ of compounds **1-4** were then obtained according to the

isodesmic reactions in Scheme 2. Obviously, these four compounds inherit high positive $\Delta_f H_{\text{gas}}^\circ$ from TTT. Among these four compounds, **4** with $-\text{N}_3$ has the greatest $\Delta_f H_{\text{gas}}^\circ$ of 439.07 kcal/mol, followed by the $-\text{NHNO}_2$ derivative (245.18 kcal/mol) and the $-\text{NO}_2$ derivative (237.78 kcal/mol). **2** with $-\text{NH}_2$ has the smallest $\Delta_f H_{\text{gas}}^\circ$ of 176.45 kcal/mol.

According to Eq. 3, the ΔH_{sub} values were predicted and presented in Table 3, which vary between 23.02 and 37.06 kcal/mol. The condensed-phase HOFs ($\Delta_f H_{\text{Cond}}^\circ$) were then obtained with Eq. 2. TTT and its derivatives in solid state have high HOFs ranging from 147.30 to 402.39 kcal/mol, which are greater than those of β -HMX (24.5 kcal/mol)⁴⁵ and ϵ -CL-20 (90.2 kcal/mol).⁴⁶ Among these compounds, **5** with $-\text{N}_3$ possesses the highest HOF of 402.39 kcal/mol. Moreover, **1** and **3** exhibit positively large HOFs of 208.37 and 207.82 kcal/mol, respectively, which are large enough to meet the requirements of energetic materials.

Electronic Structure and Stability

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are called as frontier molecular orbitals (FMOs). The energy gap (E_{gap}) between HOMO and LUMO is related to many molecular properties including kinetic stability and chemical reactivity.⁴⁷ The M06-2X/cc-pVTZ computed E_{gap} of TTT is 8.83 eV, much higher than that of BTF (6.75 eV), which is planar with three five-membered rings and one six-membered ring. The E_{gap} of compounds with $-\text{NO}_2$, $-\text{NH}_2$, $-\text{NHNO}_2$ and $-\text{N}_3$ are 7.910, 8.254, 8.256, and 7.740 eV, respectively. The TTT framework is characterized by its π -electron delocalization in the triazole and triazine rings. Every N atom in the framework forms three σ -bonds through sp^2 hybridization, making 18 p electrons including 6 π - n electrons delocalize over the framework to form a large conjugated system. Fig. 3 shows one of the π -bonding orbitals in TTT and **1**. The HOMO of TTT consists of π orbitals, and its LUMO concentrates on the nitrogen atoms in the framework and the atoms in the

substituent groups.

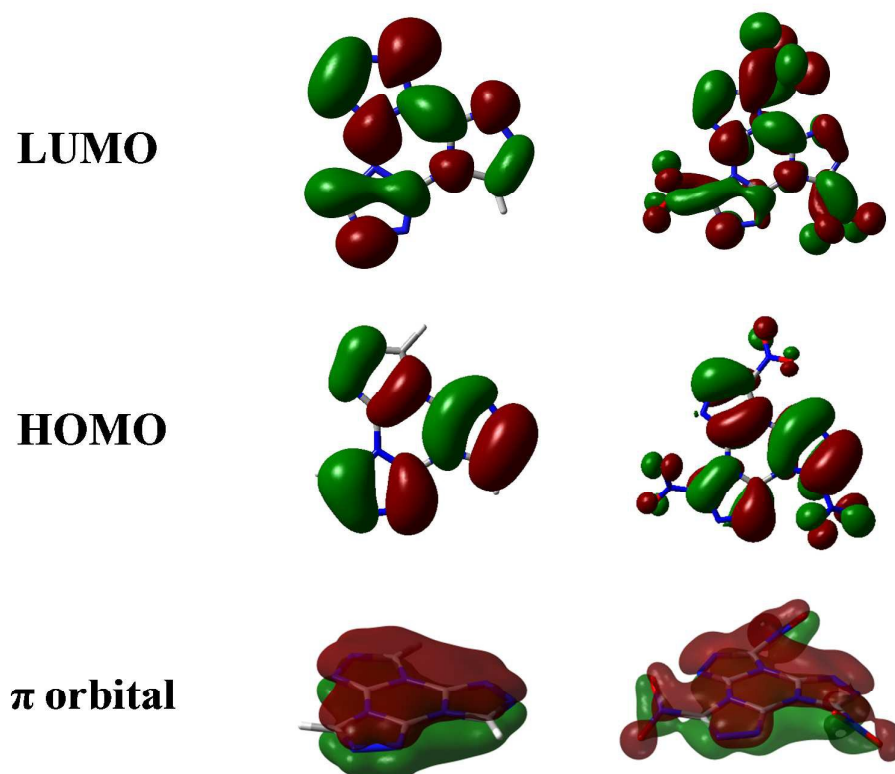


Fig. 3 HOMOs, LUMOs, and π orbitals of TTT and compound **1**.

Table 3 gives the net charge on substituent groups ($Q(R)$). In general, $Q(R)$ varies between -0.080 and $0.198 e$. It's noted that although as an electron-withdrawing group, $-N_3$ indeed transfers $0.047 e$ to framework in the participation of conjugated system.. The molecular electrostatic potential (MEP), which is related to intermolecular interaction and the impact sensitivity of the energetic compounds,⁴⁸ is definitely affected by the substituent groups. Fig. 4 illustrates the MEPs computed at the M06-2X/cc-pVTZ level for these compounds. The MEPs are scaled with color. Red denotes the most negative potential (-0.02 hartree) and blue the most positive potential (0.06 hartree). For all those compounds, the positive potential concentrates mainly on the triazine ring, while the negative potential is near to the atoms with lone-pair electrons in the five-membered rings and the substituent groups. In TTT the positive potential is at the center of the six-membered ring, while the negative

potential is around the lone pairs of the N–N structure. Along with the replacement of the hydrogen atoms with the electron-withdrawing groups, such as $-\text{NO}_2$ and $-\text{NHNO}_2$, the electrons distributed on the heterocycle decrease and leave a positive potential on the frameworks. When the electron-donating group of $-\text{NH}_2$ are incorporated in the compounds, the blue region moves to the center of six-membered rings.

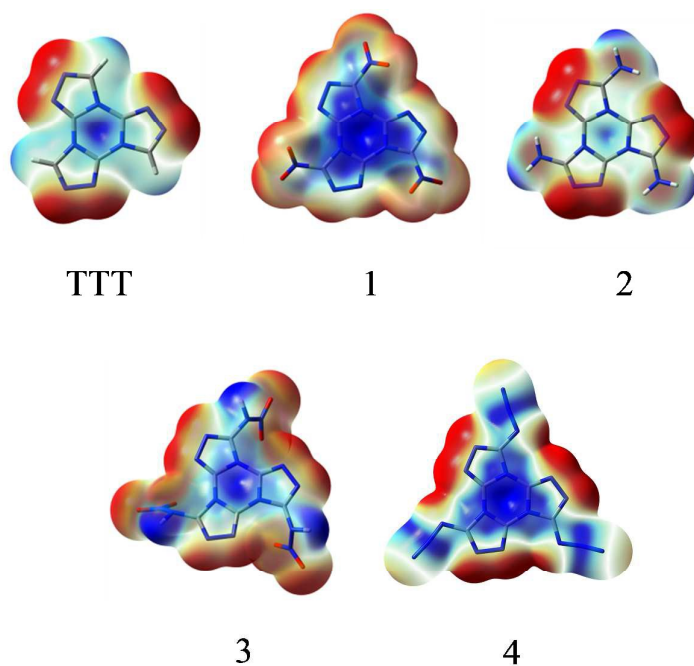


Fig. 4 The MEPs of the compounds at the M06-2X/cc-pVTZ level.

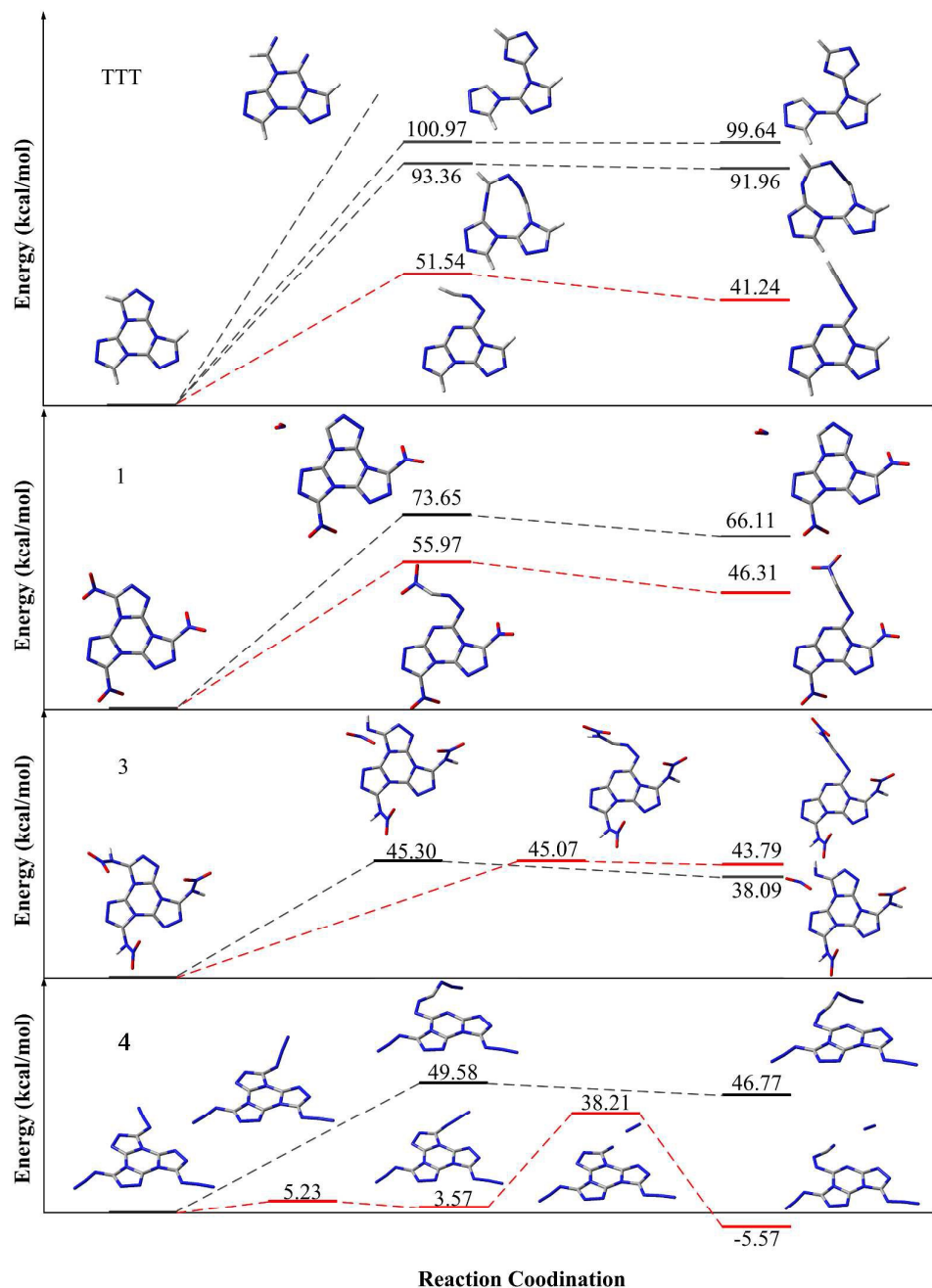


Fig. 5 The calculated initial reactions for compounds TTT, 1, 3 and 4 at the M06-2X/cc-pVTZ level.

To evaluate the kinetic stability of these compounds, the transition states were identified for breaking these weak bonds. The results are shown in Fig. 5. In TTT framework the breaking of C3–N4 bond climbs over the energy barrier of 56.21 kcal/mol, which is the lowest barrier among the reaction channels. The breaking of

N4–C6 bond has a higher barrier of 93.36 kcal/mol, and the N1–N2 bond is found difficult to break with a continuing rise of energy. In view of the energy barriers, C3–N4 breaking is the most important reaction channel for TTT. Compared to the bond breaking barriers of N–NO₂ in HMX (42.8 kcal/mol)⁴⁹ and C–NO₂ in TNT (61.7 kcal/mol)⁵⁰, one can conclude that TTT is a kinetically stable structure. The stability of TTT framework is also reflected by the other compounds. As listed in Table 4, the barriers range from 45.07 kcal/mol of –NHNO₂ derivative to 55.97 kcal/mol of –NO₂ derivative. It is evident that TTT brings a stable framework for these derivatives.

Table 4 The energy barriers for bond breaking reactions in kcal/mol

R	ΔE		ΔG	
	TS	PRO	TS	PRO
(C3–N4)				
–H	51.54	41.24	56.21	45.46
–NO ₂	55.97	46.31	61.79	51.62
–NH ₃	-	46.46	-	54.35
–NHNO ₂	45.07	43.79	55.16	53.26
–N ₃	49.58	46.77	56.49	52.96
–H(N4–C5)	93.36	91.96	97.46	96.30
–H(N4–C6)	100.97	99.64	105.35	101.55
–H(N1–N2)	-	-	-	-
–NO ₂ (C3–NO ₂)	73.65	66.11	79.60	58.44
–NHNO ₂ (N–NO ₂)	45.30	38.09	55.84	33.87
–N ₃ (N–N ₂ -1)	5.23	3.57	15.52	13.36
–N ₃ (N–N ₂ -2)	38.21	-5.57	44.27	-10.64

Furthermore, the initial decomposition reactions including the breaking of the nitro, nitramino, and azide-groups were studied. It is apparent in Fig. 5 that the barrier of C–NO₂ breaking is 73.65 kcal/mol, about 17.68–28.58 kcal/mol higher than those of C3–N4 bonds. The barrier of N–NO₂ bond is 45.30 kcal/mol, close to that of C3–N4 in **3**. For **5** with –N₃, the C3–N4 bond breaks with N₂ release and lead to a low barrier of 38.21 kcal/mol, indicating that **4** is less stable than other compounds. Therefore, compound **1** and **3** have overall good stability among these compounds.

Detonation Properties

Oxygen balance (OB) is an index to measure the deficiency or excess of oxygen in a molecule required to convert all carbon into carbon monoxide (or carbon dioxide), and all hydrogen into water. In this work, the OB values of molecules with $C_aH_bN_cO_d$ have been calculated as

$$OB (\%) = 1600 \times [d - a - b/2] / M \text{ (based on CO and HX)}. \quad ()$$

where a, b, c, d are the number of carbon, hydrogen, nitrogen and oxygen atoms in the molecule. Table 3 lists the OB values for the compounds and more than half of them possess good OB values, indicating that these compounds have a good potential to release a large amount of power.

The detonation velocity (D) and the pressure (P) are evaluated with Explo5 6.02. Fig. 6 summarizes the detonation properties of these compounds, which were obtained based on the density from crystal packing. For a comparison, D and P of the well-known explosives TNT,⁵¹ HMX,⁵¹ and CL-20⁵¹ were also presented in the figure. D and P of all these compounds are much greater than those of TNT. It is worth to note that D of **1** reaches 10.55 km/s, greater than that of CL-20. Moreover, compound **3** exhibits good performances close to HMX. Even if using the low density predicted with Eq. 4, the obtained performances of **1** and **3** are comparable to those of HMX (SI Table 1). Therefore, compound **1** and **3** promising powerful energetic materials among the C/H/N/O-containing organic compounds.

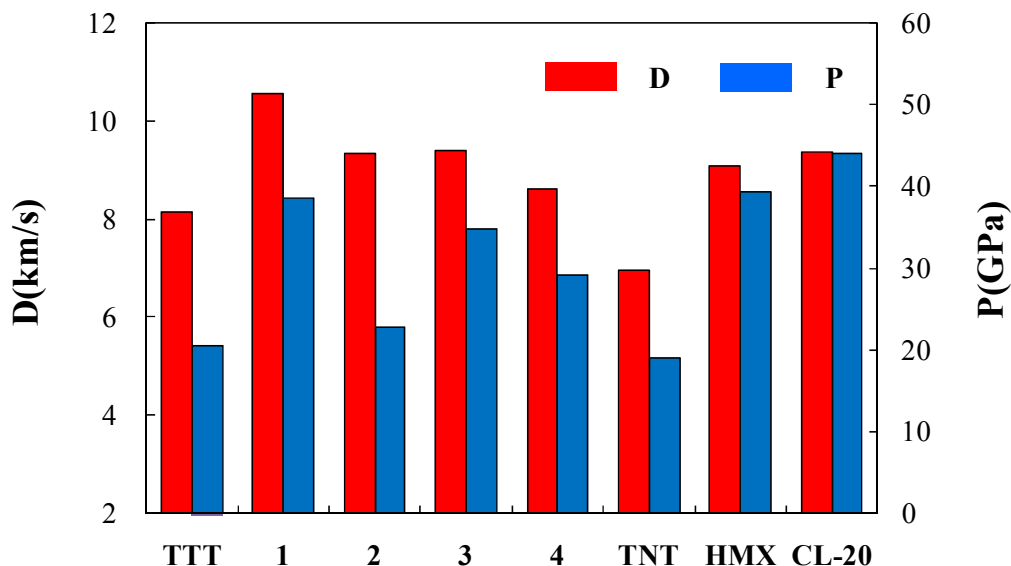


Fig. 6 Detonation parameters predicted with Explo5 for TTT, four functionalized derivatives, TNT, HMX, and CL-20.

Conclusion

In this work, a conjugated framework combining with triazole and triazine was proposed for heterocyclic energetic compounds. Tris ([1, 2, 4] triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine (TTT), and its nitro, amino, nitramino, and azide-functionalized derivatives have been studied theoretically. *Ab initio*, DFT methods were used to investigate their geometrical and electronic structure, gas and condensed-phase heat of formation. The crystal structures of these compounds were predicted with molecular packing calculations. All the compounds were predicted to possess large HOFs and high densities, which lead to great detonation performances. Compound **1** (3,7,11-trinitrotris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine, TNTTT) exhibits the remarkable D of 10.55 km/s and P of 38.57 km/s, which are better than those of HMX and CL-20. Compound **3** (N,N',N''-(tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine-3,7,11-triyl)trinitramide, TNATTT) also possesses good detonation properties ($D = 9.40$ km/s and $P = 34.78$ km/s).

Calculations on the initial decomposition reaction in gas-phase indicate that the

TTT framework is stable with high activation energies about 56 kcal/mol at the M06-2X/cc-pVTZ level, which is much higher than that of HMX. TNTTT and TANTTT were then characterized with good stability. Considering both the detonation properties and stabilities, the compounds with triazole and triazine, particularly TNTTT, are promising candidates of high-energy density material with low sensitivity and high performance.

Acknowledgements

The authors gratefully acknowledge the support of the National Natural Science Foundation of China (NO. 11402240), and the China Postdoctoral Science Foundation (No. 2014 2014M552381).

References

- 1 H. X. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377-7436.
- 2 J. H. Zhang, C. L. He, D. A. Parrish and J. M. Shreeve, *Chem.-Eur. J.*, 2013, **19**, 8929-8936.
- 3 T. M. Klapotke, F. A. Martin and J. Stierstorfer, *Angew. Chem. Int. Ed.*, 2011, **50**, 4227-4229.
- 4 P. Yin, D. A. Parrish and J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2014, **53**, 12889-12892.
- 5 P. Politzer and J. S. Murray, in *Advances in Quantum Chemistry, Vol 69*, ed. J. R. Sabin, 2014, vol. 69, pp. 1-30.
- 6 M. Joas, S. Kiessling, T. M. Klapotke, P. C. Schmid and J. Stierstorfer, *Z. Anorg. Allg. Chem.*, 2014, **640**, 2759-2765.
- 7 R. H. Wang, H. Y. Xu, Y. Guo, R. J. Sa and J. M. Shreeve, *J. Am. Chem. Soc.*, **2010**, 132, 11904-11905.
- 8 D. E. Chavez, M. A. Hiskey and D. L. Naud, *Propellants Explos. Pyrotech.*, **2004**, 29, 209-215.
- 9 G. K. Khisamutdinov, V. L. Korolev, T. N. Parkhomenko, V. M. Sharonova, E. S. Artemeva, I. S. Abdrakhmanov, S. P. Smirnov and B. I. Ugrak, *Russ. Chem. Bull.*, 1993, **42**, 1700-1702.
- 10 A. B. Sheremetev and I. L. Yudin, *Usp. Khim.*, 2003, **72**, 93-107.
- 11 Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu and S. P. Pang, *J. Am. Chem. Soc.*, 2010, **132**, 12172-12173.
- 12 A. A. Dippold and T. M. Klapotke, *J. Am. Chem. Soc.*, 2013, **135**, 9931-9938.
- 13 D. Fischer, T. M. Klapotke and J. Stierstorfer, *Angew. Chem. Int. Ed.*, 2014, **53**, 8172-8175.
- 14 P. He, J.-G. Zhang, K. Wang, X. Yin, X. Jin and T.-L. Zhang, *Phys. Chem. Chem. Phys.*, 2015, **17**, 5840-5848.
- 15 N. Kommu, V. D. Ghule, A. S. Kumar and A. K. Sahoo, *Chem.-Asian J.*, 2014, **9**, 166-178.
- 16 C. Qi, S. H. Li, Y. C. Li, Y. Wang, X. X. Zhao and S. P. Pang, *Chem.-Eur. J.*, 2012, **18**, 16562-16570.
- 17 B. Hirshberg and C. Denekamp, *Phys. Chem. Chem. Phys.*, 2013, **15**, 17681-17688.
- 18 H. X. Gao, R. H. Wang, B. Twamley, M. A. Hiskey and J. M. Shreeve, *Chem. Commun.*, 2006, 4007-4009.
- 19 V. Thottampudi, F. Forohor, D. A. Parrish and J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2012, **51**, 9881-9885.
- 20 D. Izsak, T. M. Klapotke and S. Reuter, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5641-5651.
- 21 A. A. Dippold, D. Izsak and T. M. Klapotke, *Chem.-Eur. J.*, 2013, **19**, 12042-12051.
- 22 S. Huber, D. Izsak, K. Karaghiosoff, T. M. Klapotke and S. Reuter, *Propellants Explos. Pyrotech.*, 2014, **39**, 793-801.
- 23 M. Dachs, A. A. Dippold, J. Gaar, M. Holler and T. M. Klapotke, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2171-2180.
- 24 J. T. Wu, J. G. Zhang, X. Yin, P. He and T. L. Zhang, *Eur. J. Inorg. Chem.*, 2014, **2014**, 4690-4695.
- 25 D. W. Kaiser, G. A. Peters and V. P. Wystrach, *The Journal of Organic Chemistry*, 1953, **18**, 1610-1615.
- 26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K.

- Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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. Ochtersk, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, A.01 edn., 2009.
- 27 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
- 28 T. H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007-1023.
- 29 W. Hehre, L. Radom, P. Schleyer and J. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- 30 A. G. Baboul, L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 1999, **110**, 7650-7657.
- 31 R. A. Kendall, T. H. Dunning, Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796-6806.
- 32 P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 2 edn., 1982.
- 33 E. F. C. Byrd and B. M. Rice, *J. Phys. Chem. A*, 2006, **110**, 1005-1013.
- 34 P. Politzer, J. S. Murray, M. E. Grice, M. Desalvo and E. Miller, *Mol. Phys.*, 1997, **91**, 923-928.
- 35 P. Politzer, J. Martinez, J. S. Murray and M. C. Concha, *Mol. Phys.*, 2010, **108**, 1391-1396
- 36 B. M. Rice and E. F. C. Byrd, *J. Comput. Chem.*, 2013, **34**, 2146-2151.
- 37 T. Lu and F. W. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
- 38 M. Sućeska, EXPLO5 6.02 program, Zagreb, Croatia, 2014.
- 39 Materials Studio 6.0, Accelrys, Inc., San Diego, CA, 2011.
- 40 R. Srinivasan, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1992, **48**, 917.
- 41 N. Y. Chernikova, V. K. Belsky and P. M. Zorkii, *J. Struct. Chem.*, 1990, **31**, 661.
- 42 K. A. Hofmann and O. Ehrhart, *Berichte der deutschen chemischen Gesellschaft*, 1911, **44**, 2713-2717.
- 43 V. A. Tartakovsky, A. E. Frumkin, A. M. Churakov and Y. A. Strelenko, *Russ. Chem. Bull.*, 2005, **54**, 719-725.
- 44 M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48**, 23.
- 45 P. J. Linstrom and W. G. Mallard, *NIST Chemistry WebBook*, NIST, Gaithersburg, MD, 2005.
- 46 R. L. Simpson, P. A. Urtiew, D. L. Ornellas, G. L. Moody, K. F. J. Scribner and D. M. Hoffman, *Propellants Explos. Pyrotech.*, 1997, **22**, 249-255.
- 47 B. Kosar and C. Albayrak, *Spectrochim. Acta, Part A*, 2011, **78**, 160-167.
- 48 J. S. Murray and P. Politzer, *Comp. Mol. Sci.*, 2011, **1**, 153-163.
- 49 Wu, C. J., Fried, L. E. First-Principles Study of High Explosive Decomposition Energetics. In Proceedings of the 11th International Detonation Symposium, Snowmass, CO, August 31–September 4, 1998; Office of Naval Research: Arlington, VA, 1998.
- 50 D. Furman, R. Kosloff, F. Dubnikova, S. V. Zybin, W. A. Goddard III, N. Rom, B. Hirshberg, and Y. Zeiri, *J. Am. Chem. Soc.* 2014, **136**, 4192-4200.
- 51 P. Politzer and J. S. Murray, *Cent. Eur. J. Energ. Mater.*, 2011, **8**, 209-220.