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Theoretical Study of 5,8-Dinitro-5,6,7,8-tetrahydrotetrazolo[1,5-b][1,2,4]triazine (DNTzTr)

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Abstract: The structure and properties of 5,8-Dinitro-5,6,7,8-tetrahydrotetrazolo[1,5-b][1,2,4]triazine (DNTzTr) was investigated by using quantum chemistry methods. The optimized geometry and electronic density, IR and NMR spectrum data were calculated for inspecting the electronic structure properties and nature of chemical bonds at B3LYP/6-311+G(2d) level. The critical macroscopic properties such as density, enthalpy of formation and detonation performance have been also predicted. The results show that the enthalpy of formation and density of DNTzTr are 497.64 kJ/mol and 1.82 g/cm³, respectively. The detonation velocity and pressure are 8.73 km/s and 33.97 GPa, respectively. It possesses good detonation properties and can be the potential energetic material.

Key words: physical chemistry; density functional theory; DFT; polynitro-substituted tetrazolotriazine; enthalpy of formation; detonation performance

5,8-二硝基四唑并三嗪的理论研究

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摘 要: 运用量子化学方法研究了 5,8-二硝基四唑并三嗪化合物的结构和性能。在 B3LYP/6-311+G(2d) 理论水平下, 对其进行了几何优化及计算了电子密度、IR 和 NMR, 以探究其电子结构性质和化学键本质, 预估了密度、生成焓和爆炸性能等关键参数。结果表明, 5,8-二硝基四唑并三嗪生成焓为 497.64 kJ/mol, 密度为 1.82 g/cm³, 其爆速和爆压分别为 8.73 km/s 和 33.97 GPa, 与 RDX 相当, 具有良好的爆炸性能, 有望成为潜在的含能材料。

关键词: 物理化学; 密度泛函理论; DFT; 多硝基取代四唑并三嗪; 生成焓; 爆炸性能

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Introduction

High-nitrogen heterocycles are an unique class of energetic material developed in recent years and have attracted considerable attention because of their high heat of formation, high density, and good thermal stability^[1]. Current research efforts in the energetic community are focused on developing ingredients with minimal responses to impact, friction and electrostatic discharge. Of these heterocycles, the tetrazole ring has been found to occupy the ideal middle ground on the “stability versus performance continuum” for preparation of newenergetic materials^[2].

Tetrazoles are more frequently used for the synthesis of new energetic nitrogen-rich compounds. Together with their high thermal stability and the high heat of formation(5H-1,

2,3,4-tetrazole; 237 kJ/mol), they offer a good backbone for the development of energetic compounds. Recently, many examples of energetic compounds that contain a tetrazole moiety have been investigated and synthesized^[3-6]. Of the tetrazole compounds, 1,5-diaminotetrazole (DAT) can act as a precursor for introducing the tetrazole ring synthon into a wide range of energetic materials. In 1988, Willer reported the synthesis and chemistry of the related 5,6,7,8-tetrahydrotetrazolo[1,5-b][1,2,4]triazines based on the reaction of 1,5-diaminotetrazole (DAT) with glyoxals and following the reduction. Subsequent nitration proceeded smoothly in acetic anhydridelnitric acid to give the 5,8-dinitro compound, 5,8-dinitro-5,6,7,8-tetrahydrotetrazolo[1,5-b][1,2,4]triazine, DNTzTr with six nitrogen atoms contiguously bonded and the structure was confirmed by X-ray crystallography^[7]. Howev-

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er, it is still lack of systematic and theoretical studies on the structure-property relationship on this energetic compound.

Studying the structure property relationships and using computer codes to predict the energetic properties based on molecular structure has greatly enhanced the development of new energetic materials with better performance^[1]. In this work, we firstly reported the interesting compound DNTzTr from the view of theoretical computation. The electronic structure, enthalpy of formation, density, and detonation performance of this promising polynitro energetic compound with six catenated nitrogen atoms, have been studied rigorously by high-level first-principles calculations. The present theoretical study may simulate further experimental study of these novel high-nitrogen energetic compounds including synthesis and test.

1 Computational Methods

All the calculations involved in this work were carried out using the Gaussian 09^[8] suite of programs. The geometric optimization of the target compound has been performed using the hybrid DFT-B3LYP method with the 6-311+G(2d) basis set. And the electronic density, IR spectrum, NMR and thermochemical parameters were obtained at the same levels of theory based on the optimized gas-phase structure.

Enthalpy of formation (EOF) is the most important parameter for energetic compounds. Atom equivalent schemes are used to convert quantum mechanical energies of formation of atoms to heats of formation for various classes of molecules. The gas-phase heat of formation using atom equivalents is represented as^[9]:

$$\Delta H_f(g) = E(g) - \sum_i n_i x_i \quad (1)$$

In Eq. (1), $E(g)$ is the computed minimum energy of the molecule at 0K; n_i is the number of atoms of element i and x_i is its atom equivalent energy.

We have used the x_i determined by Rice and Byrd through a least-squares fitting of Eq. (1) to the experimental $\Delta H_f(g)$ of a series of C, H, N, O-containing energetic compounds^[9].

Often the standard state of the material of interest corresponds to the condensed phase. Thus, condensed-phase enthalpy of formation can be determined using the gas-phase enthalpy of formation and enthalpy of phase transition (either sublimation or vaporization) according to Hess' law of constant heat summation^[10]:

$$\Delta H(s) = \Delta H(g) - \Delta H(\text{Sublimation}) \quad (2)$$

$$\Delta H(l) = \Delta H(g) - \Delta H(\text{Vaporization}) \quad (3)$$

Based on the electrostatic potential of a molecule through quantum mechanical prediction, the enthalpy of sublimation either vaporization can be represented as^[11]:

$$\Delta H(\text{sublimation}) = a(SA)^2 + b\sqrt{\sigma_{\text{Tot}}^2}v + c \quad (4)$$

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

Where (SA) is the molecular surface area for this structure; σ_{Tot}^2 is described as an indicator of the variability of the electrostatic potential on the molecular surface; v is interpreted as showing the degree of balance between the positive and negative potentials on the molecular surface; a , b , and c are fitting parameters. The enthalpy of formation of

title compound can be predicted on the basis of these equations.

Besides enthalpy of formation, the other critical parameter for energetic material is the crystal packing density. Considering the intermolecular interactions within the crystal, the theoretical density was obtained by an improved equation proposed by Politzer et al^[12] through the introduction of the interaction index $v\sigma_{\text{Tot}}^2$:

$$\rho = \alpha \left(\frac{M}{V(0.001)} \right) + \beta(v\sigma_{\text{Tot}}^2) + \gamma \quad (6)$$

In Eq. (6), M is the molecular mass in g/mol and $V(0.001)$ is the volume, in cm^3/mol , that is encompassed by the 0.001 au contour of the molecule's electronic density. The index $v\sigma_{\text{Tot}}^2$, defined by Eqs. (4) and (5) earlier to determine the enthalpy of vaporization and sublimation, is obtained via the electrostatic potentials on the molecular surfaces. The coefficients α , β and γ were assigned by fitting Eq. (6) to the experimental densities of a diverse group of 36 energetic compounds^[12].

The empirical Kamlet-Jacob equations^[13], widely employed to evaluate the energy performance of energetic compounds were used to estimate the detonation velocity and detonation pressure of title compound. Empirical Kamlet-Jacobs equations can be written as follows:

$$D = 1.01 (\overline{NM}^+ Q^+)^+ (1 - 1.30\rho) \quad (7)$$

$$p = 1.558\rho^2 \overline{NM}^+ Q^+ \quad (8)$$

Where D is the detonation velocity (km/s); p is the detonation pressure (GPa); N is the moles of detonation gases per gram explosive; \overline{M} is the average molecular weight of these gases; Q is the heat of detonation (kJ/g); and ρ is the loaded density of explosives (g/cm^3).

In practice, the loading density can only be approximated to a value less than the theoretical density, thus the D and p values obtained from Eqs. 7 and Eqs. 8 can be regarded as their upper limits.

2 Results and Discussions

2.1 Molecular geometry

The geometry of DNTzTr has been optimized using various first-principles methods including HF and B3LYP, and the basis sets include the split-valence types 6-31G(d), 6-311G(d), 6-311+G(2d)^[14-15]. Some bond distances optimized at various levels of theory compared with the experimental values^[7] are listed in Table 1. And the most stable molecule conformation of the title compound is shown in Fig. 1.

As shown in Fig. 1, the geometrical parameters of DNTzTr are not sensitive to the basis sets used in the optimization for B3LYP methods and the change of bond length is always less than 0.001 nm. And the optimized values from 6-311+G(2d) basis sets are significantly different from those obtained by other basis sets. However, the geometrical parameters do depend on the methods. Using the HF method, most of the calculated distances of N-N and C-N bonds are shorter than the experimental data, while the distances of C-C, O-N and C-H bonds are a little longer than that of experiment. Thus the results calculated by

B3LYP method are close to those of the experiment compared with the HF method, implying that the dynamical electron correlation plays a key role for the molecule of our concern. Therefore, we performed all geometrical and electronic calculations of title compound by B3LYP method with 6-311+G(2d) basis sets. The whole main body of molecule is made of the tetrazole and triazine ring structure with polynitro as energetic groups, which contributes to the explosive performance.

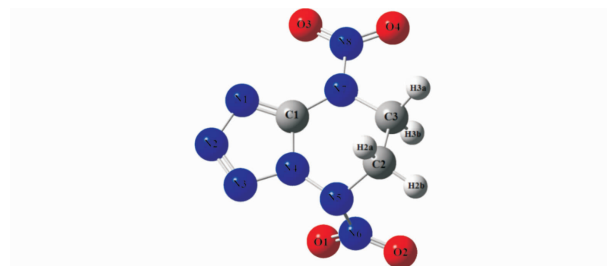


Fig. 1 The optimized geometry of DNTzTr

Table 1 Selected bond length of DNTzTr at HF and B3LYP as well as the experimental values (nm)

Bond	Bond length/nm					Bond	Bond length/nm				
	HF	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(d)	B3LYP/ 6-311+G(2d)	Exp. [7]		HF	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(d)	B3LYP/ 6-311+G(2d)	Exp. [7]
N1—N2	0.1434	0.1379	0.1379	0.1377	0.1385	C2—C3	0.1529	0.1532	0.1532	0.1525	0.1527
N2—N3	0.1262	0.1281	0.1281	0.1275	0.1287	C3—N7	0.1488	0.1474	0.1474	0.1474	0.1482
N3—N4	0.1400	0.1366	0.1366	0.1363	0.1360	N6—O1	0.1241	0.1216	0.1216	0.1210	0.1210
N4—C1	0.1361	0.1367	0.1367	0.1363	0.1357	N6—O2	0.1216	0.1207	0.1207	0.1201	0.1205
C1—N1	0.1289	0.1313	0.1313	0.1308	0.1314	N8—O3	0.1225	0.1212	0.1212	0.1206	0.1221
N4—N5	0.1378	0.1372	0.1372	0.1369	0.1384	N8—O4	0.1251	0.1225	0.1225	0.1220	0.1224
N5—N6	0.1464	0.1507	0.1507	0.1505	0.1498	C2—H2a	0.1075	0.1091	0.1091	0.1087	0.0990
C1—N7	0.1369	0.1384	0.1384	0.1382	0.1386	C2—H2b	0.1079	0.1096	0.1096	0.1092	0.0990
N7—N8	0.1388	0.1421	0.1421	0.142	0.1391	C3—H2a	0.1077	0.1093	0.1093	0.1089	0.0990
N5—C2	0.1492	0.1479	0.1479	0.1476	0.1483	C3—H2b	0.1073	0.1088	0.1088	0.1084	0.0990

2.2 Electronic structure

In general, most molecules have portions that are relatively electron rich and others that are correspondingly electron poor and a variety of atomic and molecular properties can be expressed in terms of the electrostatic density population. Using the Multiwfn program^[16] calculating density, the contour line maps of electronic density on the title compound are visualized in Fig. 2.

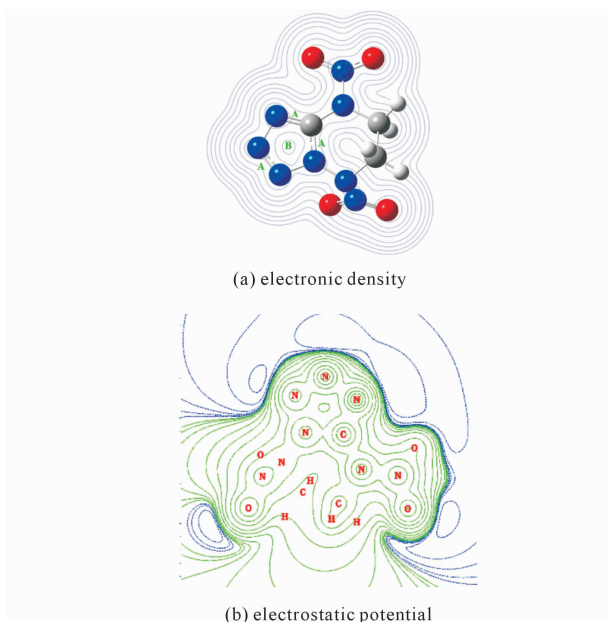


Fig. 2 Contour line map on DNTzTr

As shown in Fig. 2 (a), the heavy nucleus have high peaks

caused by nuclear charge improving electron aggregation and then display integral exponential attenuation towards all around. It is obvious that electron density surrounding the oxygen and nitrogen atom is higher than that of other atoms due to the strong electronegativity. Some origins with either positive or negative contribution from electrons should be noticed and marked in different majuscules (as shown in cyan). As we know, the electrons prefer to assemble in the bonding area (such as A) because of electron pair sharing between atoms with covalence interaction. And the delocalization mainly occurs in tetrazole ring (as marked B), which may improve the stability of the ring skeleton as well as molecular structure.

The electrostatic potential can be regarded as, effectively, another fundamental determinant of chemical reactivity and molecular interactive behavior^[17]. And the contour line map of electrostatic potential defined by the x - y plane are shown in Fig. 2(b). The nuclei naturally display the positive electrostatic potential on the molecule. In addition, the strong negative regions of potential are shown in the ring nitrogen, which is initially attracted to the electrophiles. And some of them also show the characteristic weaker negative region of potential around the oxygen atoms. Overall, the positive and negative potentials are delocalized inside and outside the rings, respectively. Such a structural characteristic is very helpful for the molecular packing via strong π - π stacking interactions.

2.3 Vibration analysis and NMR

The calculate IR spectrum of the title compound is shown

in Fig. 3.

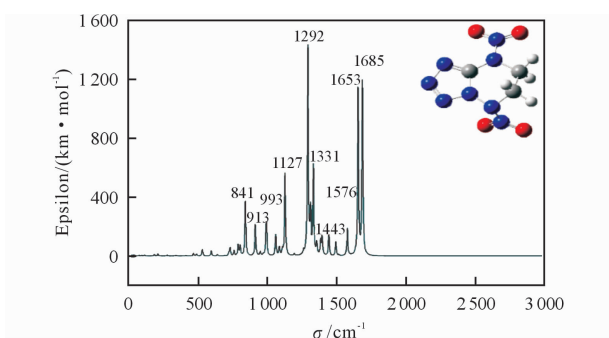


Fig. 3 Calculated IR spectrum of DNTzTr

As shown in Fig. 3, the strong IR peaks at 1685 cm^{-1} and 1653 cm^{-1} corresponds to the asymmetrical stretching modes of the nitro groups. And the stretching vibrations on C—N bonds and N—N bonds of the tetrazole and triazine ring are expected in the region 1576 , 1443 and 1227 cm^{-1} , 993 cm^{-1} . Again the peaks at 1331 and 1292 cm^{-1} refer to symmetrical stretching, while the weak peaks at 841 cm^{-1} is belonging to the scissor vibration mode of nitro groups.

Table 2 Detonation parameters for common explosives and DNTzTr

Species	$\Delta_f H_{298\text{K}}(\text{s})/(\text{kJ} \cdot \text{mol}^{-1})$	$Q/(\text{kJ} \cdot \text{g}^{-1})$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$D/(\text{km} \cdot \text{s}^{-1})$	p/GPa	$OB/\%$
TNT ^[19]	-63.12	308	1.64	6.95	19.00	-74.00
RDX ^[19]	79.00	357	1.80	8.75	34.70	-21.62
PETN ^[19]	-128.70	360	1.77	8.30	33.50	-10.12
DNTzTr	497.64	362	1.82	8.73	33.97	-29.63

It is seen that the title compound possesses a very high solid-phase enthalpy of formation derived from the large number of inherently energetic C—N and N—N bonds of high-nitrogen molecules. DNTzTr has the most positive enthalpy of formation (497.64 kJ/mol) among the common energetic compounds, and has high density with the value of 1.82 g/cm^3 , which is higher than other energetic compounds such as TNT, RDX and PETN. The heat of detonation as another property of DNTzTr is about 362 kJ/g , which become the highest one among all compounds. Detonation velocity and detonation pressure as two very important performance parameters for an energetic compound are compared in Table 3. The title compound shows relatively higher detonation velocity ($D=8.73\text{ km/s}$) than TNT and PETN, even close to remarkable explosive RDX. Again the detonation pressure ($p=33.97\text{ GPa}$) is much higher than that of TNT and similar to PETN. Overall, the compound DNTzTr possesses good detonation properties and can be a potential energetic material.

3 Conclusions

(1) 5, 8-dinitro-5, 6, 7, 8-tetrahydrotetrazolo[1, 5-b][1, 2, 4]triazine(DNTzTr), containing six catenated nitrogen atom chains was studied by using first-principles quantum

Large, systematic theoretical investigations only allow for reliable error estimates if appropriate experimental studies, such as gas-phase NMR measurements on smaller molecular systems are available^[18]. The theoretical chemical shifts of C and H in ppm in ^1H and ^{13}C NMR relative to Me_4Si and chemical shifts of N in ^{15}N NMR to MeNO_2 , have been calculated as well. And the results show that, ^1H NMR: 3.40 (H2a), 5.25 (H2b), 4.41 (H3a), 3.67 (H3b); ^{15}N NMR: -163.29 (N1), -7.98 (N2), -70.43 (N3), -271.37 (N4), -267.86 (N5), -45.97 (N6), -312.67 (N7), -68.72 (N8); ^{13}C NMR: 156.00 (C1), 41.92 (C2), 47.32 (C3). We included the calculated IR and NMR for easier assignment and positive identification of the DNTzTr.

2.4 Predicted properties

The detonation parameters for energetic compounds have been calculated including the detonation heat (Q), detonation velocity (D) and pressure (p), and enthalpy of formation (EOF), density (ρ) as well as oxygen balance (OB) values of the title molecule along with three famous explosives for comparison and systemic information are listed in Table 3.

chemistry methods. The optimized structure is made of the tetrazole and triazine ring with polynitro as energetic groups. The electronic density provides a visual representation of the chemically active sites.

(2) The calculated IR and NMR spectrum data have been performed for easier assignment and positive identification of the target compound.

(3) The compound DNTzTr possesses the most positive enthalpy of formation ($497.64\text{ kJ} \cdot \text{mol}^{-1}$) and highest density (1.82 g/cm^3) among the common energetic compounds. And with good detonation parameters ($D=8.73\text{ km/s}$, $p=33.97\text{ GPa}$), the compound DNTzTr can be the potential energetic material.

Reference:

- [1] Gao H, Shreeve J M. Azole-based energetic salts [J]. Chemical Reviews, 2011, 111(11): 7377-7436.
- [2] Fischer D, Klapötke T M, Piercey D G, et al. Synthesis of 5-aminotetrazole-1-N-oxide and its azo derivative: a key step in the development of new energetic materials [J]. Chemistry-A European Journal, 2013, 19(14): 4602-4613.
- [3] Liu Z, Wu Q, Zhu W, et al. Theoretical study of energetic trinitromethyl-substituted tetrazole and triazine derivatives [J].

- Journal of Physical Organic Chemistry, 2013, 26 (11): 939-947.
- [4] Klapötke T M, Martin F A, Stierstorfer J. N-bound primary nitramines based on 1,5-diaminotetrazole [J]. Chemistry-A European Journal, 2012, 18(5): 1487-1501.
- [5] Klapötke T M, Krumm B, Martin F A, et al. New azidotetrazoles: structurally interesting and extremely sensitive [J]. Chemistry-An Asian Journal, 2012, 7(1): 214-224.
- [6] Hiskey M A, Goldman N, Stine J R. High-nitrogen energetic materials derived from azotetrazolate [J]. Journal of Energetic Materials, 1998, 16(2-3): 119-127.
- [7] Willer R L, Henry R A. Tetrazolo[1,5-b][1,2,4]triazines: an alternate synthesis and chemistry [J]. The Journal of Organic Chemistry, 1988, 53(22): 5371-5374.
- [8] Frisch M J, Trucks G W, Schlegel H B, et al. [CP/CD]// Gaussian 09 (Revision A. 01); Gaussian, Inc., Wallingford CT, 2009.
- [9] Byrd E F, Rice B M. Improved prediction of heats of formation of energetic materials using quantum mechanical calculations [J]. The Journal of Physical Chemistry A, 2006, 110(3): 1005-1013.
- [10] Atkins P W. Physical Chemistry [M]. Oxford: Oxford University Press, 1982.
- [11] Murray J S, Politzer P. Quantitative treatment of solute/solvent interactions[C]// Theoretical and Computational Chemistry. Elsevier: Amsterdam, 1994.
- [12] Politzer P, Martinez J, Murray J S, et al. An electrostatic interaction correction for improved crystal density prediction [J]. Molecular Physics, 2009, 107(19): 2095-2101.
- [13] Kamlet M J, Jacobs S J. Chemistry of Detonation. I. A Simple method for calculating detonation properties of C, H, N, O explosives [J]. Journal of Chemical Physics, 1968, 48: 23-35.
- [14] Ditchfield R, Hehre W J, Pople J A. Molecular orbital theory of bond separation [J]. Journal of Chemical Physics, 1971, 54: 724-728.
- [15] Frisch M J, Pople J A, Binkley J S. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets [J]. Journal of Chemical Physics, 1984, 80: 3265-3269.
- [16] Lu T, Chen F. Multiwfn: A multifunctional wavefunction analyzer [J]. Journal of Computational Chemistry, 2012, 33(5): 580-592, <http://Multiwfn.codeplex.com>.
- [17] Politzer P, Murray J S. The fundamental nature and role of the electrostatic potential in atoms and molecules [J]. Theoretical Chemistry Accounts, 2002, 108(3): 134-142.
- [18] Auer A A. High-level ab-initio calculation of gas-phase NMR chemical shifts and secondary isotope effects of methanol [J]. Chemical Physics Letters, 2009, 467(4): 230-232.
- [19] Politzer P, Murray J S. Some perspectives on estimating detonation properties of C, H, N, O compounds [J]. Central European Journal of Energetic Materials, 2011, 8(3): 209-220.

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