

Molecular Design and Performance Studies of 4-(1,2,4-Triazole-5-yl) Furazan Derivatives as Promising Energetic Materials^①

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ABSTRACT In this paper, eight 4-(1,2,4-triazole-5-yl) furazan (TZFZ) derivatives were designed, and the molecular configurations of TZFZ compounds were optimized by using the B3LYP/6-311+G* level. Meanwhile, the detonation performance, density, impact sensitivity, heat of formation and oxygen balance have been investigated. The results clearly and intuitively illustrate that the introduction of -NO₂ and coordination oxygen plays a pivotal role in increasing the density and heat of formation. In summary, the properties of these compounds are better than the traditional explosives RDX and TNT, especially the density and detonation pressure. Energetic evaluations showed that compounds B1 ($P = 36.73$ GPa; $D = 8.98$ km s⁻¹, $\rho = 1.88$ g cm⁻³) and B7 ($P = 38.51$ GPa; $D = 9.17$ km s⁻¹, $\rho = 1.90$ g cm⁻³) could be seen as promising candidates of energetic insensitive compounds with remarkable performance.

Keywords: density functional theory, 4-(1,2,4-triazole-5-yl)furazan derivatives, performance prediction, molecular design; DOI: 10.14102/j.cnki.0254-5861.2011-3061

1 INTRODUCTION

Low sensitivity and high energy are two important directions in energetic materials research. Furazan and triazole compounds have always been the hotspots of research in many energetic structural units^[1, 2], because the high-nitrogen and low-hydrocarbon contents not only make them have higher density, but also easily achieve oxygen balance^[3]. The 1,2,4-triazole derivatives synthesized by Jin et al. have high detonation performance and excellent stability^[4]. The study by Du et al. also proved the good performance of furoxan compounds^[5].

In the design of high-energy materials, high-density explants play a key role because they can significantly increase the density and molecular stability of the material^[6-8]. Nitro group has been widely investigated as a substituent group in the synthesis of HEDMs, which can significantly

increase the density and improve the oxygen balance, thereby increasing the enthalpy of formation. Xu et al.^[9] reported the synthesis and characterization of 4-(1,2,4-triazole-5-yl) furazan derivatives, which firmly believed that the more nitro groups, the higher density of the energetic material and the higher enthalpy of formation. In addition, the introduction of coordinated oxygen also provides a new way for the development of energetic materials. Compared with furazan or isofurazan, the furoxan structural unit has more excellent comprehensive properties. It was found that the density of compound could be increased by 0.06 ~ 0.08 g cm⁻³ by replacing one nitril with one furoxanyl, and the corresponding detonation speed can be increased by more than 0.3 km s⁻¹^[10]. The physicochemical properties of 3,3'-bis(5-tetrazole)-4,4'-azofuroxon and 3,3'-bis(5-tetrazole)-4,4'-azofurazan are shown in Fig. 1.

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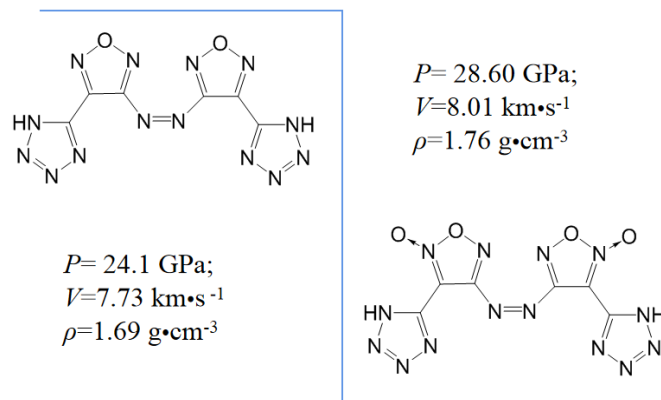


Fig. 1. Performance comparison of azofuroxon and azofurazan

In order to find high-performance, low-sensitivity energetic materials, we designed to connect the high nitrogen-rich triazole and furazan (or furazan oxide) as the parents. Thus, $-\text{NO}_2$, $-\text{NHNO}_2$, $-\text{CH}(\text{NO}_2)_2$ and $-\text{C}(\text{NO}_2)_3$ are selected to design eight groups of compounds (Fig. 2), including B1 ~ B3

without coordination oxygen and B4 ~ B8 with coordination oxygen. Density functional volume-based thermodynamic calculations and density functional theory (DFT) are adopted to select the energetic compounds with high energy and good stability.

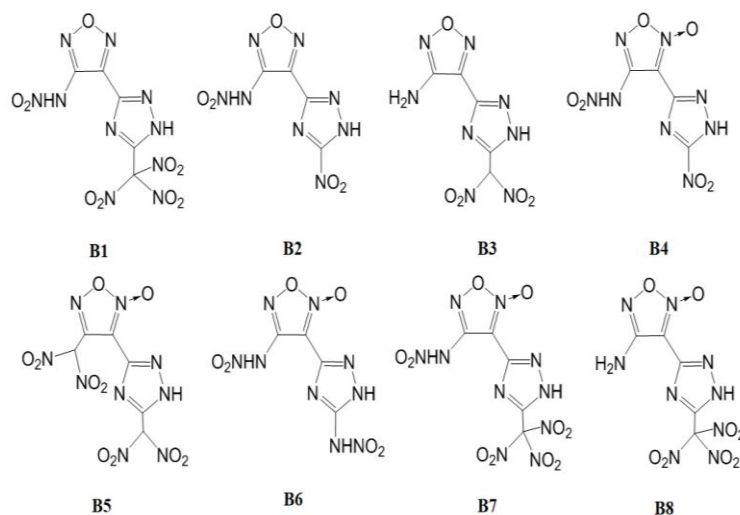


Fig. 2. Newly designed 4-(1,2,4-triazole-5-yl) furazan derivatives

2 COMPUTATIONAL METHODS

In this work, all calculations were carried out by using the Gaussian 09^[11] suite of programs. The B3LYP/6-311+G* method was used to optimize the structure of the compound. The most stable structures were determined by frequency analysis and calculation. The highest occupied molecular orbitals-the lowest unoccupied molecular orbitals (HOMO-LUMO) and electronic density, and thermodynamic parameters were calculated at the same level of theory.

Poltz et al.^[12, 13] proposed to improve the density prediction of crystal structure by modifying electrostatic

interactions, in which the interaction index $\nu\sigma^2_{Tot}$ was introduced. This article follows their calculation method, and the formula is as follows:

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

where M is the molecular mass (g mol^{-1}); $V(0.001)$ is the volume of the isolated gas molecule ($\text{cm}^3 \text{mol}^{-1}$), which is encompassed by the 0.001 au contour of the electronic density; $\nu\sigma^2_{Tot}$ is the product of the electrostatic balance coefficient and the total variance of the electrostatic potential, derived from the molecular electrostatic potential calculation; the coefficients α , β , and γ are 0.9183, 0.0028, and 0.0443,

respectively.

The empirical Kamlet-Jacobs^[14-16] equations were widely used to estimate the values of D and P for the high energy materials containing C, H, O and N as the following equations:

$$D = 1.01(\overline{NM}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (2)$$

$$P = 1.558\rho^2\overline{NM}^{1/2}Q^{1/2} \quad (3)$$

where D is the detonation velocity (km s^{-1}); P the detonation pressure (GPa); N the moles of detonation gases per gram explosive; \overline{M} the average molecular weight of these gases; Q the heat of explosion (cal g^{-1}), defined as the difference of the heat of formation between products and reactants; and ρ the loaded density of explosives (g cm^{-3}).

Impact sensitivity is a deterministic factor that determines whether explosives can be used safely^[17]. Rice and Hare^[18] used the performance-structure relationship method (generalized interaction property function) to estimate the impact sensitivity $h_{50\%}$ of the explosives.

$$h_{50\%} = 29.3 + 1.386 \times 10^{-3} \times \exp[48.84 \cdot \nu] \quad (4)$$

where ν is the electrostatic balance coefficient calculated by the Multiwfn^[19] program.

The enthalpy of formation reflects the basic thermodynamic

properties of energetic compounds. In this paper, the atomization energy method is selected to calculate the enthalpy of formation as shown in Eq. (5)^[20], which converts the quantum mechanical energy of atoms into the heat of formation (HOF) of molecules^[21, 22].

$$HOF(g) = E(g) - \sum n_i x_i \quad (5)$$

3 RESULTS AND DISCUSSION

3.1 Molecular structure

The optimization of TZFZ compounds was completed by using the hybrid B3LYP functional with the 6-311+G* basis set. The optimized structure is shown in Fig. 3. The vibration frequency analysis shows that there is no virtual frequency, which indicates that the optimized structure is a minimum point on the potential energy surface and is a stable configuration.

The adjacent furazan and triazole rings are practically planar. When coordinated oxygen is present, the dihedral angles are almost constant and almost coplanar. This implies that the conjugation effect of furoxan and triazole rings is strong, which helps to increase the stability of the molecule.

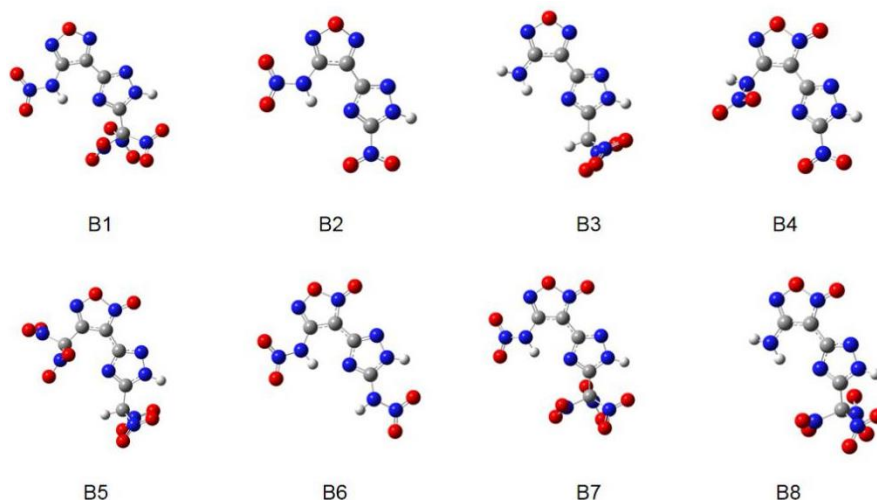


Fig. 3. Optimized molecular structures of 4-(1,2,4-triazole-5-yl) furazan derivatives

The bond lengths of C–N of the triazole ring skeleton are between typical C=N (1.29 Å) and C–N (1.47 Å). The N–N bonds range from N–N (1.45 Å) to N=N (1.25 Å), and close to the double bond length, indicating that the triazole ring has conjugation. The lengths of two N–O bonds in the furazan ring without coordinating oxygen are within the normal range of N–N bond. What's more, the two N–O bonds are approximately equal in length. The N–O bond distance outside the furazan ring is within the normal range of

nitrogen-oxygen double bond. On the contrary, the two N–O bonds in the ring are quite different. One is significantly longer than the normal N–O bond, which is obtained by introducing coordinated oxygen on the furazan ring. It may be thus concluded that the stability of the compound will decrease when the furazan ring becomes a furoxan ring.

Among all TZFZ compounds, the bond angles (C(1)–N(1)–C(2), N(2)–N(3)–C(2)) of the triazole ring skeleton are between 101° and 110°, which belong to the range of ring

bonds. When the N→O coordination bond is introduced on the furazan ring, the bond angles are basically unchanged except for the significant changes in the N–O–N bond angle (decrease by about $3^\circ \sim 4^\circ$).

3.2 Electronic structure

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are called frontier molecular orbitals. The energy gap between HOMO and LUMO, which determines the chemical reactivity, kinetic stability and optical polarizability of the molecule, was calculated by using Multiwfn program^[18, 23, 24]. E_{HOMO} , E_{LUMO} and energy gap ΔE are listed in Table 1. It can be seen from

Fig. 4 that the orbital loops on HOMO and LUMO overlap, with the red color representing the positive phase and the green color showing the negative one. The larger the energy gap value, the more stable the molecule^[18]. Under the same circumstances, the introduction of nitro group will reduce the energy gap and reduce the stability of the compound. The ΔE value (4.04 eV) of B6 indicates that -NHNO₂ group is beneficial to reduce the activity of the compound, because the nitro group is usually the main cause of the reaction as the number of nitro groups increases. The more unstable the compound is, the more active it is.

Table 1. Calculated HOMO and LUMO Energies and Energy Gap (ΔE) of the 4-(1,2,4-Triazole-5-yl) Furazan Derivatives

Compounds	E (eV)		ΔE (eV)
	HOMO	LUMO	
B1	-8.37	-4.77	3.60
B2	-8.33	-4.35	3.99
B3	-7.21	-4.21	3.00
B4	-7.78	-3.96	3.82
B5	-7.99	-4.42	3.56
B6	-7.52	-3.49	4.04
B7	-7.80	-4.77	3.03
B8	-7.05	-4.56	2.50

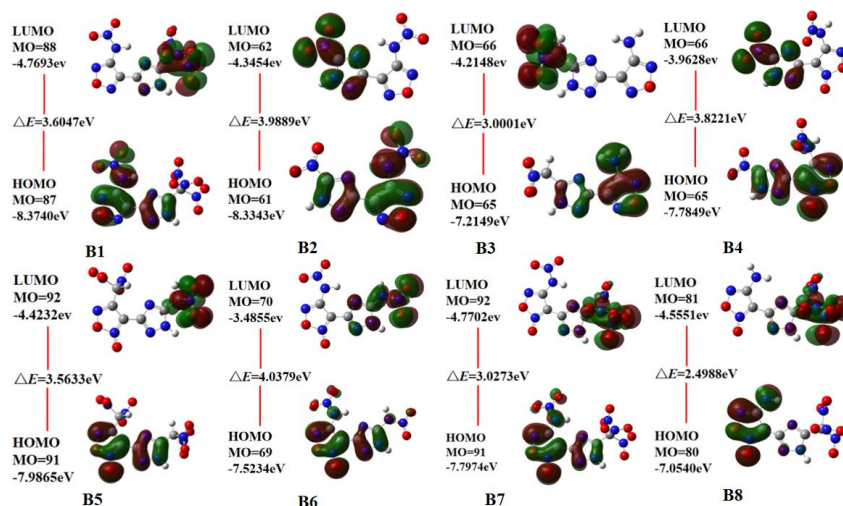


Fig. 4. HOMO-LUMO orbitals of 4-(1,2,4-triazole-5-yl) furazan derivatives (B1~B8)

3.3 Detonation properties

Table 2 lists the calculated values of Q , D , P and oxygen balance (OB) of B1 ~ B8 molecules. Meanwhile, the experimental detonation performances of two well-known

explosives trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) are also listed in this table. Comparing with the performance of famous explosives can help us understand the various properties of the designed compounds.

Table 2. Detonation Parameters of 4-(1,2,4-Triazole-5-yl) Furazan Derivatives

Compounds	ρ (g cm ⁻³)	<i>HOF</i> (kcal mol ⁻¹)	<i>Q</i> (kcal mol ⁻¹)	<i>D</i> (km s ⁻¹)	<i>P</i> (GPa)	<i>OB</i> ^a (%)	<i>h</i> _{50%} (cm)
B1	1.88	494.14	1595	8.98	36.73	-9.25	38
B2	1.82	366.41	1852	8.96	35.82	-42.73	32
B3	1.84	449.59	1459	8.51	32.58	-26.43	51
B4	1.82	447.39	1549	8.64	33.31	-18.60	30
B5	1.85	341.17	1573	8.75	34.50	-15.51	29
B6	1.81	482.08	1514	8.65	33.32	-20.50	34
B7	1.90	487.28	1650	9.17	38.51	-4.42	35
B8	1.87	423.22	1556	8.84	35.42	-17.66	56
TATB ^b	1.93	-74.61	1149	7.86	31.50	-55.81	490 ^c
TNT ^b	1.64	-63.12	1295	6.95	19	-73.97	98 ^c

^aOxygen balance for C_aH_bO_c, *OB*/% (1600(c - 2a - b/2)/MW) (MW, molecular weight).^bThe calculated values of TATB and TNT are taken from Ref. [13] and [27], respectively.^cThe experimental values of TATB and TNT are taken from Ref. [17].

The density of the compounds is between 1.81 (g cm⁻³) ~ 1.90 (g cm⁻³), which far exceeds the density of TNT. Among them, B1, B7 and B8 have the highest density, which is close to 1.90 g cm⁻³ because of the addition of -C(NO₂)₃. The introduction of furoxan ring can also increase the crystal density of the molecule, because when the N atom on the furazan ring is oxidized, the entire molecular structure will be tighter, and the increase in molar volume is less than the increase in molar mass^[25].

The enthalpy of formation is one of the important parameters of energetic materials. The enthalpy changes of the compounds designed in this paper are all positive values, which are higher than those of traditional explosives. By comparing the contribution of several different formation enthalpies, it is found that when -NH₂ is added, the formation enthalpy of the compound will be reduced. When the substituent is -NHNO₂, the enthalpy of formation of the compound can be increased. Through comparison, it can also be found that the contribution of different energetic groups to the enthalpy of formation is as follows: -C(NO₂)₃ > -NHNO₂ > -NO₂ > -NH₂. Consistent with previous reports, the value of *HOF* improved significantly as the number of nitrogen atoms in the energy-containing molecule increased.

Oxygen balance is closely related to explosive sensitivity and strength^[26]. The calculation of oxygen balance lays the foundation for further understanding and research of these

compounds.

The detonation velocity (*D* = 32.58 ~ 38.51 km s⁻¹) and detonation pressure (*p* = 8.51 ~ 9.17 GPa) are calculated by the Kamlet-Jacobs formula, which is significantly better than the traditional compounds. It can be found from the formula that the detonation velocity and detonation pressure are closely related to the formation enthalpy and density of the compound. Generally, the higher the formation enthalpy and density, the higher the detonation velocity and detonation pressure. However, there are exceptions, such as compounds B3 and B6, indicating that density is not always the decisive factor.

The drop height *h*_{50%} can reflect the sensitivity of explosives^[17], and the *h*_{50%} value is inversely proportional to the sensitivity^[27, 28]. Due to the existence of strong electron withdrawing groups such as -C(NO₂)₃, -NHNO₂, -NO₂, etc., its stability is reduced to a certain extent. In contrast, B3 and B8 are relatively stable.

The comparison between *P*, *D* and *OB* of all compounds and common explosives TATB and TNT is shown in Fig. 5. The *P* and *D* of all compounds are significantly better than TATB and TNT, and they have better oxygen balance values. In all cases, the density of compounds B1 and B7 is the highest, and the oxygen balance is the closest to ideal. Therefore, they may become potentially high-energy insensitive explosives.

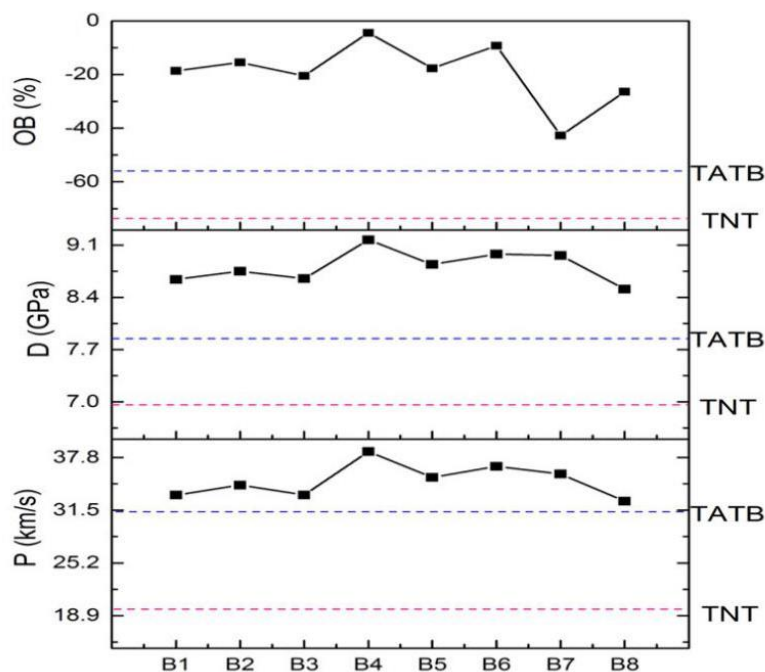


Fig. 5. P , D and OB of 4-(1,2,4-triazole-5-yl) furazan derivatives

4 CONCLUSION

In this study, we designed and optimized a series of 4-(1,2,4-triazole-5-yl) furazan derivatives. On this basis, we have calculated density, $HOFs$, detonation properties and oxygen balance. Through the calculation of physicochemical and energetic properties, the following conclusions can be drawn: The properties of the compound with furoxan structure were obviously better than that of the common furazan structure. The introduction of $-C(NO_2)_3$ and furazan oxide ring has a good effect on the density improvement. It is

interesting to note that when the substituent is $-NH_2$, the enthalpy of formation of the compound can be reduced. On the contrary, when the substituent is $-NHNO_2$, the enthalpy of formation of the compound can be increased. The results clearly and intuitively illustrate that it is a useful way to increase the detonation performance by introducing $-NO_2$. In summary, the TZFZ compounds have high detonation velocities ($D = 8.51 \sim 9.17 \text{ km s}^{-1}$) and detonation pressures ($P = 32.58 \sim 38.51 \text{ GPa}$). In summary, B1 and B7 are expected to be the promising candidates of HEDMs.

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