



Computational Investigation on the Structure and Performance of Novel 4,7-dinitro-furazano-[3,4-*d*]-pyridazine Derivatives

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Abstract: Seven novel energetic 4,7-dinitro-furazano-[3,4-*d*]-pyridazine derivatives were designed, and their optimized structures and performances were studied by density functional theory (DFT) at B3LYP/6-311g(d,p) level. The detonation performances were estimated by the Kamlet-Jacobs equations. The results show that these compounds have high crystal densities (1.818-1.925 g·cm⁻³), detonation velocities (8.51-9.56 km·s⁻¹) and detonation pressures (32.28-41.70 GPa). The bond dissociation energies (BDEs) of the weakest bond (N–O bond) vary from 70.889 kJ·mol⁻¹ to 173.283 kJ·mol⁻¹, and some of them exhibit higher BDEs than that of RDX (N–NO₂ bond, 149.654 kJ·mol⁻¹) and HMX (N–NO₂ bond, 154.905 kJ·mol⁻¹). M4 and M5 exhibit similar and higher detonation performance than RDX (8.81 km·s⁻¹, 34.47 GPa). The detonation performance of M7 (9.56 km·s⁻¹, 41.70 GPa) even surpasses that of HMX (9.10 km·s⁻¹, 39.00 GPa). Otherwise, the specific impulse values of M1-M7 (266-279 s) outperform HMX (266 s) by 0-13 s, which indicates that M1-M7 may show better performance as monopropellants. It is concluded that density, heat of formation, stability, detonation performance and specific impulse of the designed compounds depend on the position and number of the N→O oxidation bonds.

Keywords: 4,7-dinitro-furazano-[3,4-*d*]-pyridazine, heat of formation, density, detonation performance, bond dissociation energy

1 Introduction

It has been a huge challenge in the area of energetic materials to achieve a fine balance between good detonation performance and safety, therefore,

the preparation of new insensitive high-energy density materials (HEDM) has become a developing target of energetic materials [1, 2]. In recent years, furazan and furoxan compounds have become powerful skeletons for novel HEDMs due to their high heats of formation (ΔH_f), good thermal stabilities, high densities and high amounts of active oxygen [3, 4]. Therein, the representative compounds include 3,4-bis(3-nitrofurazano-4-yl)furoxan (DNTF, $\rho = 1.86 \text{ g}\cdot\text{cm}^{-3}$, $D=8930 \text{ m}\cdot\text{s}^{-1}$), 4,4'-oxybis(3-nitro-1,2,5-oxadiazole) (FOF-1, $\rho = 1.907 \text{ g}\cdot\text{cm}^{-3}$, $D=8930 \text{ m}\cdot\text{s}^{-1}$), 4,4'-oxybis(3-(fluorodinitromethyl)-1,2,5-oxadiazole) (FOF-13, $\rho = 1.92 \text{ g}\cdot\text{cm}^{-3}$, $D = 8497 \text{ m}\cdot\text{s}^{-1}$) and (*E*)-1,2-bis(4-nitro-1,2,5-oxadiazol-3-yl) diazene oxide (DNAF, $\rho = 2.02 \text{ g}\cdot\text{cm}^{-3}$, $D = 10000 \text{ m}\cdot\text{s}^{-1}$) [5-7]. However, in spite of the excellent densities and detonation performances, their application is restricted by the conflict between energy and safety. Therefore, it is necessary to continue the search for new insensitive high-energy density furazan and furoxan derivatives.

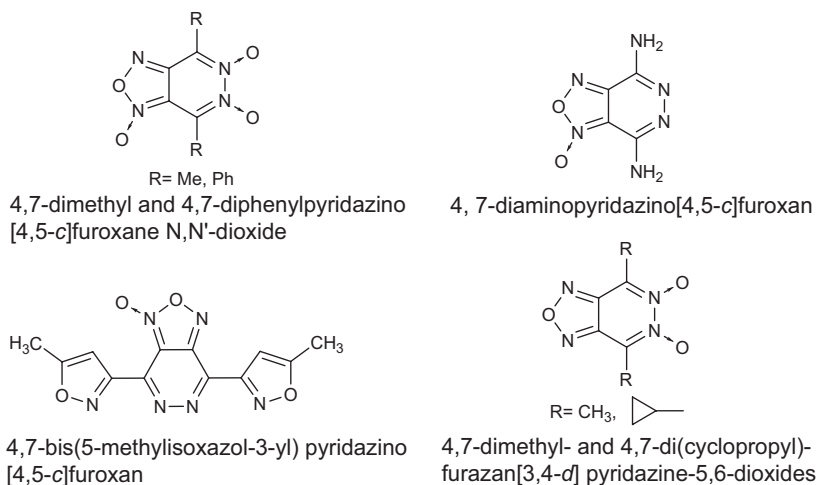


Figure 1. Illustration of furazano-[3,4-*d*]-pyridazine derivatives

Recently, furazano-heterocycles have aroused great interest from explosive researchers because of their unique conjugated structures and better stability. For example, Zhou *et al.* [8] proved that benzotrifuroxan shows excellent detonation performance and safety compared with HMX. Liu *et al.* [9] reported the synthesis of 4*H*,8*H*-bis-furazano[3,4-*b*:3',4'-*e*]pyrazine-4,8-diylbis(methylene)dinitrate, which possess excellent energetic properties ($\rho = 2.00 \text{ g}\cdot\text{cm}^{-3}$, $D = 9067 \text{ m}\cdot\text{s}^{-1}$, $P = 43 \text{ GPa}$) and stability (thermal decomposition temperature: 250.5 °C). Some studies have been carried out with the preparation of furazano-[3,4-*d*]-

pyridazine derivatives [10-13], such as 4,7-dimethyl- and 4,7-diphenyl-pyridazino[4,5-*c*]furoxane *N,N'*-dioxide, 4,7-diaminopyridazino[4,5-*c*]furoxan, 4,7-bis(5-methylisoxazol-3-yl)pyridazino[4,5-*c*]furoxan, 4,7-dimethyl- and 4,7-di(cyclopropyl)- furazan[3,4-*d*]pyridazine-5,6-dioxides (Figure 1). However, the relationship between molecular structure and energetic performance for furazano-[3,4-*d*]pyridazine compounds is still unclear.

Because the synthesis and testing of novel HEDM is a costly and lengthy process, it seems that theoretical investigation is an ideal choice for screening before attempting any synthetic work [14-16]. As a result, experimental synthesis can be designed and performed better and more efficiently based on theoretical investigations. The density functional theory (DFT) method has been well-established and successfully used to investigate the structure and properties of energetic materials. Pan *et al.* [17] studied the structure and performance of furazano[3,4-*b*]pyridazine-based derivatives by using DFT. Wei *et al.* [18] used DFT to investigate energetic tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine and 1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine derivatives.

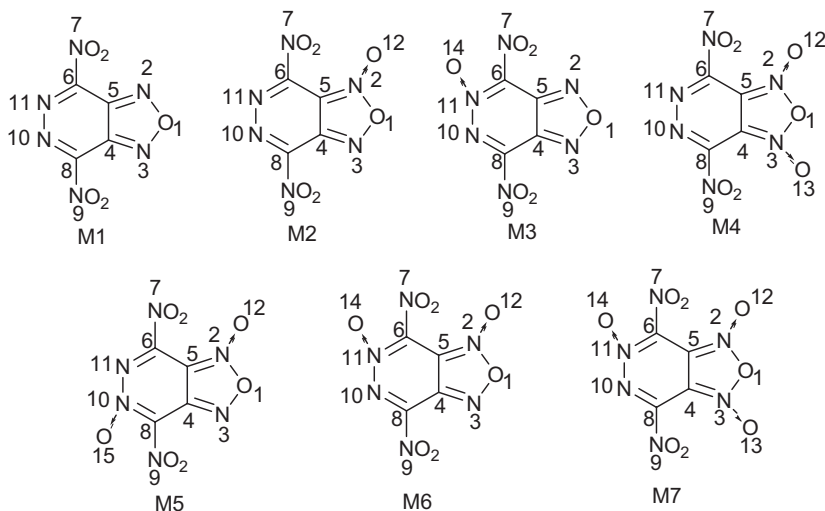


Figure 2. Illustration, with atom numbering of the designed compounds

It is generally considered that the introduction of the N→O functionality to nitrogen-containing heterocycles influences their performance [19-22] as follow: firstly, it can improve the density and ΔH_f value; secondly, it can supply more active oxygen and decrease the demand for oxygen; finally, it may impair the stability. For the above-mentioned reasons, seven energetic materials based on

4,7-dinitro-furazano-[3,4-*d*]-pyridazine with the introduction of N→O bonds were designed as shown in Figure 2, and their molecular and explosive properties were studied by the DFT method at B3LYP/6-311g(d,p) level. It was anticipated that the results would be able to provide valuable information about the value of synthesising furazano-[3,4-*d*]-pyridazine compounds.

2 Computational Methods

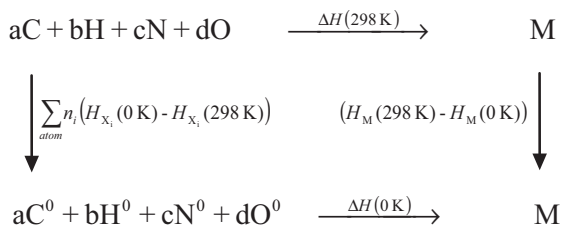
Structural optimizations of the designed compounds were performed at B3LYP/6-311g(d,p) level in the Gaussian 09 quantum chemical package [23]. Previous studies have proved that this method and the basis set were reliable for predicting the structure and performance of energetic materials [24, 25]. All of the optimized structures were characterized to be true relative energy minima of the potential surfaces by frequency calculation (no imaginary frequencies were found). Based on the optimized structures, other relative properties, such as heats of formation (ΔH_f), bond dissociation energies (BDEs), Wiberg bond orders (BO), molecular electrostatic potentials (MESP) and detonation performance of the designed compounds were calculated and are discussed below.

In this work, the crystal densities of the compounds were evaluated by Equation 1, which was developed by Politzer *et al.* [26]. The volumes of the title compounds were defined as inside a contour of 0.001 electrons/bohr³ density, estimated using a Monte Carlo integration [17, 27, 28], then the average volumes were estimated by performing 100 single-point energy calculation for each optimized structure.

$$\rho = \alpha' \left(\frac{M}{V} \right) + \beta' (v\sigma_{\text{tot}}^2) + \gamma' \quad (1)$$

where M is the molecular mass ($\text{g}\cdot\text{mol}^{-1}$), V is the average volume ($\text{cm}^3\cdot\text{mol}^{-1}$), v is a measure of the balance between positive and negative potentials on the molecular surface, and σ_{tot}^2 represents the variability of the electrostatic potential. α' , β' and γ' are fitting parameters and are taken from Ref. [26].

The atomization approach was applied to evaluate the gas phase ΔH_f ($\Delta H_f(\text{g}, 298 \text{ K})$) of the designed compounds. Jing *et al.* [29] has also efficiently obtained the ΔH_f values of energetic nitrogen-rich N,N' -azobispolynitrodiazoles by using the atomization approach. The atomization approach [1, 29, 30] for estimating the ΔH_f is as follows:



Scheme 1. The atomization scheme

where n_i stands for the number of atoms of X_i in M , $H_{X_i}(0\text{ K})$ stands for ΔH_f of X_i at 0 K, and $\Delta H(0\text{ K})$ can be derived from $H_{X_i}(0\text{ K})$. $(H_{X_i}(0\text{ K}) - H_{X_i}(298\text{ K}))$ and $(H_M(298\text{ K}) - H_M(0\text{ K}))$ represent the enthalpy correction for the molecule (M) and atom (X_i) between 0 K and 298 K, respectively, and they can be performed by the Gaussian 09 package.

The gas phase heat of formation of M at 298 K ($\Delta H_f(\text{g}, 298\text{ K})$) can then be written as Equation 2:

$$\Delta H_f(\text{g}, 298\text{ K}) = \Delta H_f(0\text{ K}) + \sum_{atom} n_i (H_{X_i}(0\text{ K}) - H_{X_i}(298\text{ K})) + (H_M(298\text{ K}) - H_M(0\text{ K})) \quad (2)$$

Finally, the gas phase heat of formation was estimated by our own computer code. The specific equation is:

$$\Delta H_f(\text{g}, 298\text{ K}) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (3)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPEs) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 K to 298 K. ΔnRT is the work term for the reactions of an ideal gas. For the isodesmic reactions here, $\Delta nRT = 0$.

However, the solid state ΔH_f is much more accurate, compared with the gas phase ΔH_f , in evaluating the detonation performance of energetic materials because it determines the final detonation properties [30]. These can be estimated by Equations 4 and 5, reported by Politzer and Byrd [26, 31-33]:

$$\Delta H_f(\text{s}, 298\text{ K}) = \Delta H_f(\text{g}, 298\text{ K}) - \Delta H_{\text{sub}}(298\text{ K}) \quad (4)$$

$$\Delta H_{\text{sub}}(298\text{ K}, \text{kJ}\cdot\text{mol}^{-1}) = \alpha(A_s)^2 = \beta(\sigma_{\text{tot}}^2)^{0.5} + \gamma \quad (5)$$

where ΔH_{sub} is the sublimation enthalpy, α , β and γ are fitting parameters and adopted from Ref. [33], A_s is the molecular surface.

The BDE is regarded as a quite convincing index for molecular stability [27, 34], and means the difference between the energy of a molecule and those of the radicals produced when a bond in the molecule is broken. It is important to understand the pyrolysis mechanism of the compound [35-37]. The BDE of the molecule, corresponding to the enthalpy of reaction which is required for homolytic bond cleavage at 298 K and 1 atm, was evaluated [34, 38-40] by the following Equation 6:

$$\text{BDE(R-X)} = \text{E(R}\cdot\text{)} + \text{E(X}\cdot\text{)} - \text{E(R-X)} \quad (6)$$

where E is the total electronic energy, R-X is the designed molecule, and R. and X. are the radicals produced when the trigger bond is broken.

The BDE with zero point energy correction (BDE_{ZPE}) is:

$$\text{BDE}_{\text{ZPE}}(\text{R-X}) = \text{BDE(R-X)} + \Delta\text{ZPE} \quad (7)$$

where ΔZPE is the zero point energy correction.

The impact sensitivity can be measured by the height (H_{50}) which a standard weight falling upon the explosive gives a 50% probability of initiating explosion. Keshavarz *et al.* [41] put forward a simple and appropriate approach to calculate H_{50} of energetic materials as follows, Equation 8 I:

$$\log H_{50} = \frac{46.2923a + 35.6305b - 7.7005c + 7.9425d + 44.4167n_{(-\text{CNC}-)} + 102.2749n_{(-\text{CNNC}-)}}{M} \quad (8 \text{ I})$$

where a , b , c and d are the number of carbon, hydrogen, nitrogen and oxygen atoms, respectively, $n_{(-\text{CNC}-)}$ and $n_{(-\text{CNNC}-)}$ are the numbers of $-\text{CNC}-$ and $-\text{CNNC}-$ moieties in the aromatic ring, and M is the average molecular weight.

However, using Equation 8 I, it is difficult to distinguish the impact sensitivities of isomers. Cao and Gao [42] put forward a simple and appropriate approach to distinguish the impact sensitivities (H_{50}) of isomers, as follows, Equation 8 II:

$$H_{50} = 0.1926 + 98.64Q_{\text{NO}_2}^2 - 0.03405 \text{ OB} \quad (8 \text{ II})$$

where $Q_{\text{NO}_2}^2$ is the net charge of the nitro groups in the compounds, OB is the oxygen balance (%), [for $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$: $\text{OB} = 1600 \times (d - 2a - b/2)/M_w$], and M_w is the molecular weight.

The electric spark sensitivity of energetic compounds can be regarded as a parameter for electrostatic discharge, and a reliable method has been used to predict the electrostatic sensitivity of nitroaromatic energetic compounds [43], as follows, Equation 9:

$$E_{ES}(J) = 4.60 - 0.733a + 0.724d + 9.16r_{b/d} - 5.14C_{R,OR} \quad (9)$$

where a , b and d are the numbers of carbon, hydrogen and oxygen atoms in $C_aH_bN_cO_d$, respectively, $r_{b/d}$ is the ratio of hydrogen to oxygen atoms and $C_{R,OR}$ is the number of certain groups such as alkyl (R) or alkoxy (OR) groups attached to an aromatic ring.

The detonation performances were estimated by the widely used empirical Kamlet-Jacobs equations [44]:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2} (1+1.3\rho) \quad (10)$$

$$P = 1.559NM^{1/2}Q^{1/2}\rho^2 \quad (11)$$

where D is the detonation velocity ($\text{km}\cdot\text{s}^{-1}$), P is the detonation pressure (GPa), ρ is the density of the explosive ($\text{g}\cdot\text{cm}^{-3}$), N is the amount of gaseous detonation products per gram of explosive ($\text{mol}\cdot\text{g}^{-1}$), M is the average molecular weight of the gaseous products ($\text{g}\cdot\text{mol}^{-1}$), and Q is the chemical energy of the detonation ($\text{cal}\cdot\text{g}^{-1}$), which can be derived from the ΔH_f values of the products and reactants.

The specific impulse (I_{sp}) is used to evaluate the energy efficiency of propellant combustion. The unit of the specific impulse is seconds. Its value is of utmost significance for the determination of the propellant mass necessary to meet the ballistic requirements. However, the specific impulse of an energetic compound depends on its structural parameters. Keshavarz put forward a new method for calculating the specific impulse based on the structural parameters of energetic compounds, as follows, Equation 12 [44]:

$$I_{sp} = 2.421 - 0.0740a - 0.0036b + 0.0237c + 0.0400d - 0.1001n_{\text{NH}_2, \text{NH}} + 0.1466(n_{\text{Ar}} - 1) \quad (12)$$

where a , b , c and d are the number of carbon, hydrogen, nitrogen and oxygen atoms in $C_aH_bN_cO_d$, respectively, I_{sp} is the specific impulse in $\text{N}\cdot\text{s}\cdot\text{g}^{-1}$ and the units are ultimately converted into s, $n_{\text{NH}_2, \text{NH}}$ is the number of NH_2 and NH groups, and n_{Ar} is the number of aromatic rings in aromatic explosives.

3 Results and Discussion

3.1 Molecular geometries

Table 1. Selected bond lengths, bond angles and dihedral angles of the optimized structures of the designed compounds from calculations at B3LYP/6-311G(d,p) level

Bond length [Å]	M1	M2	M3	M4	M5	M6	M7
O(1)–N(2)	1.359	1.497	1.378	1.471	1.460	1.539	1.513
N(2)=C(5)	1.317	1.345	1.317	1.336	1.346	1.338	1.376
C(5)–C(6)	1.427	1.417	1.416	1.423	1.411	1.412	1.366
C(6)=N(11)	1.288	1.290	1.355	1.288	1.282	1.351	1.416
O(1)–N(3)	1.359	1.346	1.348	1.470	1.368	1.328	1.439
N(3)=C(4)	1.317	1.313	1.313	1.336	1.314	1.312	1.360
C(4)–C(8)	1.427	1.434	1.425	1.423	1.422	1.429	1.403
C(8)=N(10)	1.288	1.286	1.278	1.288	1.353	1.277	1.324
N(10)–N(11)	1.375	1.375	1.433	1.379	1.430	1.431	1.427
C(8)–N(9)	1.498	1.494	1.504	1.493	1.468	1.501	1.481
C(6)–N(7)	1.498	1.495	1.470.	1.493	1.502	1.470	1.470
Bond angle [°]							
N(2)–O(1)–N(3)	114.245	110.181	113.822	107.119	110.167	109.452	104.372
C(5)=N(2)–O(1)	103.870	103.413	103.812	105.805	104.274	102.808	109.041
C(4)=N(3)–O(1)	103.870	106.281	104.219	105.813	105.972	106.83	107.333
C(6)=N(11)–N(10)	120.667	120.037	120.955	120.379	118.610	120.666	121.352
C(8)=N(10)–N(11)	120.657	120.821	119.308	120.377	121.142	119.210	119.994
C(5)–C(6)=N(11)	123.057	123.026	119.587	123.428	124.187	119.586	118.541
C(4)–C(8)=N(10)	123.057	123.684	124.155	123.427	120.159	124.882	123.600
C(4)–C(5)–N(2)	109.005	107.718	108.584	110.613	107.833	107.836	109.394
C(5)–C(4)–N(3)	109.010	112.399	109.563	110.612	111.744	113.044	109.696
Dihedral angles [°]							
C(6)–C(5)=N(2)–O(1)	-178.061	-178.665	178.674	-177.074	179.488	178.844	-177.976
C(8)–C(4)=N(3)–O(1)	178.066	176.844	178.662	177.082	179.023	179.877	178.974

The molecular frameworks of the designed compounds are presented in Figure 2 and their structures have been optimized at B3LYP/6-311g(d,p) level. Based on the optimized structures, selected bond lengths, bond angles and dihedral angles are analyzed and listed in Table 1. The O(1)–N(2), N(2)=C(5), C(5)–C(6) and C(6)=N(11) bond lengths of M1 are shorter than typical single bonds but longer than double bonds, respectively, which indicates these bonds in the furazan ring and the pyridazine ring are conjugated. In addition, it is obvious that O(1)–N(2) and N(10)–N(11) bond lengths of M2–M7 are longer than those

of M1 when N→O oxidation bonds are introduced to the furazan or pyridazine rings, which suggests that N→O oxidation may impair stability. Otherwise, the incorporation of N→O oxidation has few effects on the bond angles of the designed compounds and their structures still remain stable. Meanwhile, the dihedral angles C(6)–C(5)=N(2)–O(1) and C(8)–C(4)=N(3)–O(1) vary within $\pm 4^\circ$, indicating that the compounds exhibit excellent coplanarity, and there is still good conjugation between the furazan and pyridazine rings. Therefore, the designed compounds still possess good stability despite N→O oxidation decreasing the conjugation.

3.2 Heat of formation

Table 2. The calculated heats of formation of the designed compounds

Comp.	Area [Å ²]	$v\sigma^2$ [kcal/mol]	ΔH_{sub} [kJ·mol ⁻¹]	$\Delta H_f(\text{g})$ [kJ·mol ⁻¹]	$\Delta H_f(\text{s})$ [kJ·mol ⁻¹]	$\Delta H_f(\text{s}) \times 10^{-3}$ [kJ·kg ⁻¹]
M1	190.543	19.932	97.832	587.113	489.281	2.308
M2	199.527	21.195	105.672	559.041	453.369	1.988
M3	199.182	21.488	105.676	544.338	438.662	1.924
M4	208.783	16.901	108.672	567.363	458.691	1.880
M5	207.622	24.902	115.208	574.029	458.821	1.880
M6	208.780	20.570	112.268	550.250	437.982	1.795
M7	215.763	24.169	126.701	620.519	493.818	1.899
Furazan	95.367	34.262	57.903	199.746(196.27 ^a)	141.843	2.026
Triazole	99.444	89.238	89.874	273.404(267.03 ^a)	183.530	2.660
Tetrazole	94.218	80.701	84.024	341.757(332.46 ^a)	257.733	3.682
Tetrazine	106.689	28.219	57.661	491.329(481.57 ^a)	433.668	5.289
5-AzTT	188.428	87.392	137.711	914.490(859.5 ^b)	776.779(779.5 ^b)	4.363
1-AzTT	188.387	76.456	132.558	943.370(898.9 ^b)	810.812(819.0 ^b)	4.555
RDX	–	–	–	–	191.63 ^c	0.875
HMX	–	–	–	258.15 ^c	–	0.872

^a These values are from Refs. [52, 53].

^b These values are from Ref. [54].

^c These values are from Ref. [35].

High positive ΔH_f values and high densities are often emphasized for HEDMs [46]. The ΔH_f values of the designed compounds, and of 5-AzTT (5-(5-azido-1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole) and 1-AzTT (1-(5-azido-1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole) are listed in Table 2. The computational ΔH_f values of four basic heterocycles, 5-AzTT and 1-AzTT approximate to their reference values, which shows that the automation approach is reliable in this work. The title compounds have good positive gas phase ΔH_f values (544.338 kJ·mol⁻¹ to 620.519 kJ·mol⁻¹)

and solid phase ΔH_f values (437.982 kJ·mol⁻¹ to 493.818 kJ·mol⁻¹) compared with those of RDX ($\Delta H_f(s) = 191.63$ kJ·mol⁻¹) and HMX ($\Delta H_f(g) = 258.15$ kJ·mol⁻¹). However, the ΔH_f value per unit mass reflects more accurately the energy content of the energetic compounds than that per mole. As shown in Table 2, M1 possesses the highest ΔH_f value, which shows that the ΔH_f values of the title compounds are decreased by introducing N→O oxidation. Furthermore, M4 and M5 have smaller ΔH_f values than M2 and M3 when a second N→O oxidation bond is introduced. This may indicate that the ΔH_f value will still decrease if two N→O oxidation bonds are incorporated into M1. In addition, M4-M6 possess two N→O oxidation bonds, and their ΔH_f values decrease as follow: M4 ≈ M5 > M6, which suggests that the position of the N→O oxidation bond has an effect on the ΔH_f value. However, M7 possesses a larger ΔH_f value compared with M4-M6 but still smaller than those of M2 and M3 when a third N→O oxidation bond is introduced into M1. Consequently, the ΔH_f values of M1-M6 increase in the order: M6 < M4 ≈ M5 < M7 < M3 < M2 < M1, which may suggest that the ΔH_f value is influenced by the position and number of N→O oxidation bonds.

3.3 Molecular electrostatic potentials and frontier orbital energies

It has recently been found, and extensively used, that the computational MESP is generally related to the impact sensitivity of an energetic material. Politzer and Murray [47, 48] concluded that the positive regions are larger and stronger than the negatives ones in energetic materials. The calculated MESP of the title compounds are shown in Figure 3. It is obvious that the strongly positive MESP surface (coloured red) is outstanding in the centre of the designed compounds, while the negative MESP surface (coloured blue) results from the -NO₂ and N→O oxidation bonds on the periphery of the title compounds. The positive MESP regions are larger and stronger than the negative ones in the title compounds. Therefore, these compounds may be potential energetic materials.

The molecular frontier orbital energy and energy gap of the designed compounds are listed in Table 3. The band gap ($\Delta E = |\epsilon(\text{HOMO}) - (\text{LUMO})|$) is an important index for estimating molecular stability, especially for compounds with similar frameworks [38, 49]. A smaller energy gap means less molecular stability due to the easy electron transition from HOMO to LUMO [50, 51]. By contrast, a large ΔE indicates good stability and low sensitivity. M1 ($\Delta E = 385.95$ kJ·mol⁻¹) has the largest ΔE value, which implies the other compounds become less stable because of the introduction of N→O oxidation bonds. Comparing the band gap of M2 (333.44 kJ·mol⁻¹) with that of M4 (262.55 kJ·mol⁻¹), it can be seen that the introduction of a second N→O oxidation bond into the furazan ring

particularly decreases the stability. When a second N→O oxidation bond is incorporated into the pyridazine ring, the energy gaps of M5 (304.55 kJ·mol⁻¹) and M6 (275.68 kJ·mol⁻¹) are also reduced. In addition, M5 whose two N→O oxidation bonds lie on opposite sides, is more stable than that of M6, where they lie on the same side. M7 possesses the smallest ΔE because three N→O oxidation bonds are incorporated into M1. All ΔE values of the designed compounds are less than those of RDX and HMX.

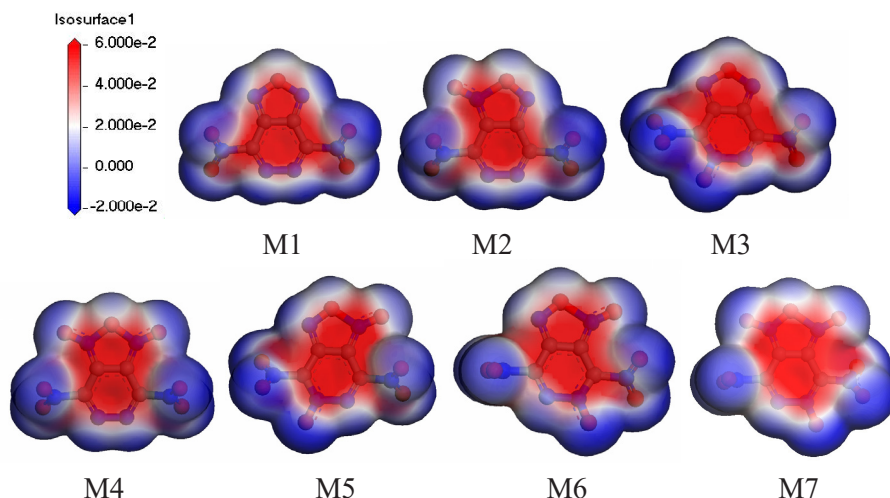


Figure 3. The 3D MESP of the designed compounds

Table 3. Total energy (E_0), zero point energy (ZPE), thermal correction to enthalpy (H_T) and the frontier orbital energy of the title molecules

Comp.	E_0 (Hartree)	ZPE [kJ·mol ⁻¹]	H_T [kJ·mol ⁻¹]	HOMO [kJ·mol ⁻¹]	LUMO [kJ·mol ⁻¹]	ΔE [kJ·mol ⁻¹]
M1	-856.878	187.72	29.41	-876.92	-490.97	385.95
M2	-932.061	196.91	32.56	-813.91	-480.47	333.44
M3	-932.060	198.49	32.29	-806.23	-480.47	325.76
M4	-1007.234	205.05	35.71	-737.77	-475.22	262.55
M5	-1007.243	208.20	34.92	-779.77	-475.22	304.55
M6	-1007.240	207.15	35.44	-745.64	-469.96	275.68
M7	-1082.394	211.52	39.38	-778.94	-523.21	255.73
5-AzzT	-663.054	235.370	27.75	-0.274	-0.081	506.72
1-AzzT	-663.068	237.343	27.70	-0.271	-0.080	501.47
RDX	-897.655	373.17	35.54	-236.899	-821.598	584.699
HMX	-1196.876	500.99	48.07	-278.933	-818.473	539.540

3.4 Bond dissociation energy and sensitivity

The stability of highly energetic explosives has been emphasized in practical applications. The computational BDEs of the trigger bond can be seen as a quantitative parameter for molecular stability [46]. In addition, the Wiberg bond order values also reflect the strength of the trigger bond [29]. A large Wiberg bond order indicates that the bond is difficult to break and thus the molecule is stable. As listed in Table 4, three possible bond cleavages have been used to study the molecular stability of the title compounds. It was observed that the position and number of the N→O oxidation bonds have an effect on the BDEs of these compounds and the N–O bond in the furazan ring is the weakest one. When introducing N→O oxidation bonds into the furazan ring in M1, the BDEs values of the N(O)–O bond (M2, M4–M7) decrease, which shows that furoxan exhibits poorer stability than furazan. This is in agreement with Refs. [52, 53]. Accordingly, M7 exhibits the lowest stability.

If the BDE value of the weakest bond in a compound is $>80 \text{ kJ}\cdot\text{mol}^{-1}$, it may be a practical energetic material; if the BDE value is $>120 \text{ kJ}\cdot\text{mol}^{-1}$, it may be regarded as an excellent energetic material, which is consistent with the stability requirements of HEDMs [46]. The calculated BDEs of the N(2)–O(1) bonds vary from $70.889 \text{ kJ}\cdot\text{mol}^{-1}$ to $173.283 \text{ kJ}\cdot\text{mol}^{-1}$, thus M1, M3 and M4 possess high BDEs and meet the stability requirements of HEDMs compared with RDX ($149.654 \text{ kJ}\cdot\text{mol}^{-1}$) and HMX ($154.905 \text{ kJ}\cdot\text{mol}^{-1}$) (Table 4). Otherwise, when introducing a further N→O oxidation bond to M2, M4 has a higher BDE than M2, M5 and M6 in accordance with the analysis of the N(O)–O bond length, which may result from electron withdrawal. However, when introducing a further N→O oxidation bond to M4, the BDE of M7 (N–O bond) particularly decreases, and is smaller than that of M5 and M6. In addition, comparing the BDEs of M1, M2 and M4 (N–N bond) with those of M3, M5 and M6, it is easy to see that the latter exhibit higher BDEs because of the incorporation of N→O oxidation bonds into the pyridazine ring. However, this is contrary to the result from bond length analysis and further study remains to be performed.

H_{50} is a complex matter for energetic compounds because it contains metastable states undergoing very rapid and highly exothermic reactions. The higher the H_{50} value, the more insensitive the compound is. As shown in Table 4 ($H_{50}(\text{I})$), when more N→O oxidation bonds are introduced into 4,7-dinitro-furazano-[3,4-d]-pyridazine, H_{50} decreases. That is to say, the compounds become more sensitive, and only the $H_{50}(\text{I})$ (cf. Equation 8 I) value of M1 is superior to that of RDX and approximates to that of HMX. The $H_{50}(\text{II})$ values (cf. Equation 8 II) are applied to distinguish isomers and their values gradually decrease slightly. Thus, the values for M2 and M3, and M5 and M6 are close to each other. This suggests that the $H_{50}(\text{II})$ values of isomers are actually

Table 4. The BDEs, Wiberg BO and H_{50} of the designed molecules

Comp.	N(9)-O(1)		N(5)-N(6)		C-NO ₂		-Q _{NO₂}	H ₅₀ [cm]		OB	E _{res} [J]
	BDE [kJ·mol ⁻¹]	Wiberg BO	BDE [kJ·mol ⁻¹]	Wiberg BO	BDE [kJ·mol ⁻¹]	Wiberg BO		I	II		
M1	173.283	1.197	191.662	1.160	201.164	0.856	-0.450	23.05	20.93	-22.64	5.29
M2	118.148	0.829	189.036	1.191	202.164	0.857	-0.451	18.49	20.73	-14.04	6.01
M3	165.407	1.109	265.176	0.999	225.793	0.842	-0.454	18.49	21.00	-14.04	6.01
M4	152.279	0.850	186.411	1.177	196.913	0.853	-0.434	16.46	18.99	-6.56	6.74
M5	105.020	0.879	232.650	1.000	225.793	0.841	-0.458	16.46	21.11	-6.56	6.74
M6	94.518	0.766	238.921	0.996	199.538	0.842	-0.451	16.46	20.48	-6.56	6.74
M7	70.889	0.533	149.654	0.957	199.538	0.757	-0.428	14.87	18.26	0	7.46
RDX	–	–	–	–	149.654	0.977	-0.415	19.45(28 ^d)		-62.92	1.98
HMX	–	–	–	–	154.905	0.783	-0.483	23.94(32 ^d)		-62.92	2.69

^dThese values are from Ref. [55].Note: H_{50} (I) and H_{50} (II) see Equations 8 I and 8 II, respectively.

approximately equal (except for M4). In addition, due to two N→O oxidation bonds being incorporated into one furazan ring, M7 shows the smallest $H_{50}(\text{II})$ value, which is consistent with the analysis of the $H_{50}(\text{I})$ value.

The electric spark sensitivity is determined experimentally by subjecting the explosive to a high-voltage discharge from a capacitor. As is shown in Table 4, the E_{ES} value is increased by introducing more N→O oxidation bonds into 4,7-dinitro-furazano-[3,4-*d*]-pyridazine, which means the compounds become more insensitive to electric spark. Meanwhile, all of the E_{ES} values of the designed compounds (5.29-7.46 J) are higher than that of HMX (2.69 J). As is shown in Figure 4, based on the computational BDEs (the main condition), H_{50} , E_{ES} , and ΔE values, it may be concluded that the molecular stability of the designed compounds decreases in the order: M1 > M3 > M4 > M2 > M5 > M6 > M7.

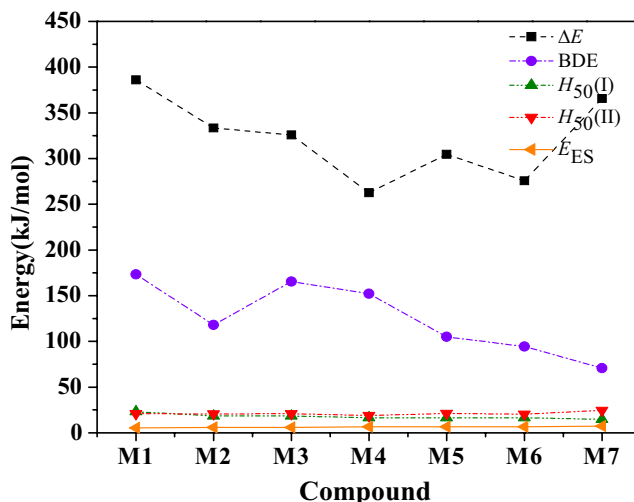


Figure 4. The BDE, ΔE , H_{50} and E_{ES} of the title compounds. (Note: the units of H_{50} is cm, the units of E_{ES} is J)

3.5 Detonation performance and specific impulse

Density is one of the most important physical properties for all energetic materials for calculating the detonation velocity and detonation pressure by the Kamlet-Jacobs procedure. A much more accurate approach developed by Politzer *et al.* [26] was applied to evaluate the densities of the title compounds and these are presented in Table 5. It can be seen that the densities of the designed compounds vary from $1.818 \text{ g}\cdot\text{cm}^{-3}$ to $1.925 \text{ g}\cdot\text{cm}^{-3}$, which approximates and even surpasses the density of RDX ($1.82 \text{ g}\cdot\text{cm}^{-3}$). The density of M7 ($1.925 \text{ g}\cdot\text{cm}^{-3}$) even surpasses that of HMX ($1.91 \text{ g}\cdot\text{cm}^{-3}$). Therefore, these compounds may possess

good detonation performance. In addition, comparing M1 with M2-M7, it is obvious that N→O oxidation makes a great contribution in enhancing the densities.

It is well known that the Kamlet-Jacobs equations have been proved to be reliable and widely used to compute the detonation performance of energetic materials [35, 36, 44]. It can be seen from Table 5 that the title compounds possess good detonation velocities of 8.93 km·s⁻¹ to 9.56 km·s⁻¹ and detonation pressures of 35.43 GPa to 41.70 GPa, which (except for those of M1) are superior to the experimental detonation performance of RDX (8.75 km·s⁻¹, 34.70 GPa). The detonation performance of M7 (9.56 km·s⁻¹, 41.70 GPa) is particularly superior to that of HMX (9.19 km·s⁻¹, 38.45 GPa). Figure 5 displays the ρ , D and P values of the designed compounds, RDX and HMX, and it is easily seen that the detonation velocities and detonation pressures of M2-M7 are considerably increased when N→O oxidation bonds are incorporated into M1. Moreover, comparing M2 and M3 with M4, M5 and M6, the latter three exhibit more excellent detonation performance because of the introduction of two N→O oxidation bonds. M7 possesses the best detonation performance, when three N→O oxidation bonds are introduced into M1, which indicates the number of N→O oxidation bonds has a great influence on the detonation performance. In addition, the explosive properties of M5 are larger than those of M6 but smaller than those of M4, suggesting the position of the N→O oxidation bonds has an influence on the explosive properties. Consequently, the detonation performance of the designed compounds increases as follows: M1 < M3 ≈ M2 < M6 < M5 ≈ M4 < M7.

Table 5. Predicted density and detonation performance of the designed compounds along with RDX and HMX

Comp.	ρ [g·cm ⁻³]	Q [cal·g ⁻¹]	D [km·s ⁻¹]	P [GPa]	I_{sp} (s)
M1	1.818	1660.68	8.51	32.28	266
M2	1.866	1712.74	8.93	35.43	270
M3	1.871	1697.33	8.93	35.46	270
M4	1.889	1798.37	9.12	37.95	274
M5	1.877	1798.50	9.12	37.47	274
M6	1.862	1778.08	9.09	36.66	274
M7	1.925	1900.856	9.56	41.70	279
5-AzTT	1.790	1042.98	7.73	26.43	–
1-AzTT	1.752	1088.67	7.70	25.87	–
RDX	1.806 (1.82 ^e)	1481.03	8.81 (8.75 ^e)	34.47 (34.70 ^e)	261(266 ^f)
HMX	1.884 (1.91 ^e)	1533.90	9.19 (9.10 ^e)	38.45 (39.00 ^e)	266(266 ^f)

^e The experimental densities and detonation velocities and pressures are from Refs. [40, 57, 58].

^f The values are from Ref. [59].

Energetic materials are not only intended to be used as explosives, but as components in advanced propellants formulations. The specific impulse (I_{sp}) is used to compare performances of rocket propellants [56]. The calculated I_{sp} values of these compounds are listed in Table 5. The remarkable I_{sp} value of M1 surpasses that of RDX and is equal to that of HMX. The I_{sp} values of M2-M6 are close to each other and outperform HMX by 4-13 s, which indicates that when more N→O oxidation bonds are incorporated into M1, the I_{sp} values of the title compounds gradually increase. In the end, a better performance may be achieved by changing from RDX and HMX to M1-M7 as monopropellants.

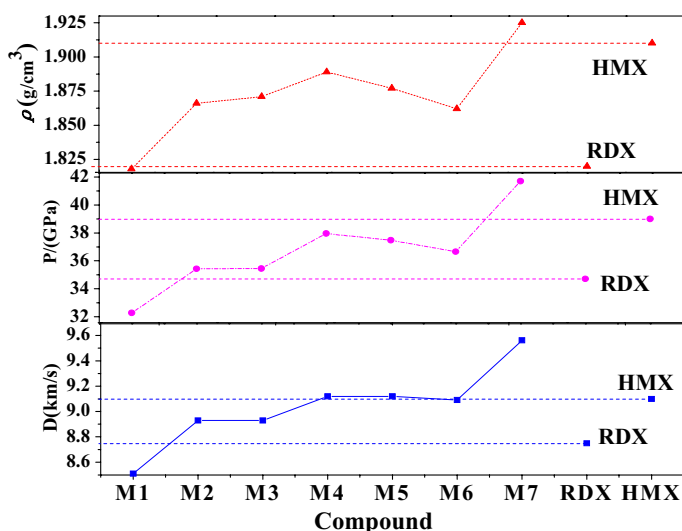


Figure 5. Density, detonation pressure, and detonation velocity of the designed compounds

4 Conclusions

A detailed study of the relationship between the structure and performance of 4,7-dinitro-furazano-[3,4-*d*]-pyridazine derivatives has been performed by the DFT method at B3LYP/6-311G(d,p) level. The main results presented are as follows:

- (1) The designed compounds exhibit very positive ΔH_f values, high densities, and good detonation performances. M2-M6 show good detonation velocity, detonation pressure and specific impulse compared with RDX and HMX. M7 even surpasses those of HMX.

- (2) The computational BDEs of the three relatively weak bonds show that the N–O bond is the weakest one and the BDEs of these compounds vary from 70.889 kJ·mol⁻¹ to 173.283 kJ·mol⁻¹. M1, M3 and M4 possess good molecular stability and are consistent with the stability requirements of HEDMs.
- (3) It was found that as the number of N→O oxidation bonds increases, the density increases, while the ΔH_f values and BDEs decrease. However, the ΔH_f value increases when a third N→O oxidation bond is introduced. In addition, M2 possesses a higher ΔH_f value, but smaller BDEs and density than M3. For M4-M6, their densities and BDEs increase in the order: M6 < M5 < M4; however, their ΔH_f values increase in the order: M6 < M4 ≈ M5. It may be concluded that the densities, ΔH_f values and BDEs of the designed compounds are influenced by the position and number of the N→O oxidation bonds.
- (4) Despite partially impairing safety, the N→O oxidation bond is a very effective functional group for improving the inadequate energetic properties of 4,7-dinitro-furazano-[3,4-*d*]-pyridazine, and confers more excellent performance.
- (5) Considering various performance characteristics, M3, M4 even M2 may be good potential candidates for HEDMs. Consequently, these compounds are worthy of further study.

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