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# Computational design of high energy density materials with zero oxygen balance: A combination of furazan and piperazine rings

He Lin[a,*], Dong-Dong Yang[a], Nan Lou[a], Shun-Guan Zhu[b], Hong-Zhen Li[c]

[a] School of Chemistry and Materials Science, Ludong University, Yantai 264025, China
[b] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[c] Institute of Chemical Materials, Chinese Academy of Engineering Physics (CAEP), Mianyang 621900, China

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ABSTRACT

The development of novel high energy density materials (HEDMs) with balanced detonation performance and sensitivity is a long-term goal in the energetic material field. In this work, by means of density functional theory, we systematically investigated physicochemical and energetic properties of three novel HEDMs constructed from furazan and piperazine frameworks with zero oxygen balance. Our results show that all these compounds have high densities (2.01–2.06 g·cm$^{-3}$), positive heats of formation (94.48–1132.95 kJ·mol$^{-1}$), excellent detonation performance (detonation velocity 9.24–9.85 km·s$^{-1}$; detonation pressure 40.33–46.47 GPa) and acceptable impact sensitivity ($H_{50}$ 26–44 cm). However, based on bond dissociation energy (BDE) calculations, it is found that only compound 1 is thermally stable. Given these properties, it could be expected compound 1 is the most promising HEDM with acceptable sensitivity. Meanwhile, in this work, it is also demonstrated that the introduction of coupled heterocyclic backbone and zero oxygen balance is an effective strategy to achieve a good balance between detonation performance and sensitivity.

## 1. Introduction

Over the past decades, to meet the increasing requirements for improved high energy density materials (HEDMs), the development of novel HEDMs with significant advantages over currently used compounds have been attended prime interest [1–5]. For the practical use, an ideal HEDM should have good oxygen balance, high density, positive heat of formation, remarkable detonation performance, favorable thermal stability, and low sensitivity toward external stimuli. Although numerous strategies have been carried out to explore potential HEDMs with a good balance between detonation performance and sensitivity, the inherent trade-off between high energy and stability seriously impedes the development of HEDMs [6].

In the recent years, furazan (1,2,5-oxidiazole) and furoxan (1,2,5-oxidiazole-2-oxide) have received great interest in the design of novel HEDMs [7–12]. Owing to a large quantity of C—N and N—O bonds in the backbones, these furazan derivatives usually exhibit favorable heats of formation. Particularly, both experimental and theoretical investigations have demonstrated that HEDMs constructed from furazan (1,2,5-oxidiazole) and furoxan (1,2,5-oxidazole-2-oxide) backbones show a good compromise between high energy and low sensitivity. For example, Solodyuk et al. synthesized 4,4′-diamino-3,3′-azoxyfurazan (DAAF, Scheme 1) via the oxidation of 3,4-diaminofurazan (DAF) with hydrogen peroxide under various conditions, and found that DAAF is an insensitive energetic material with a density of 1.747 g·cm$^{-3}$ [8]. Zhang et al. investigated the synthesis method and properties of bis(nitrofurazano)furazan (BNFF, Scheme 1), and demonstrated that BNFF possesses a high density (1.839 g·cm$^{-3}$), low melting point (82.6 °C), powerful detonation performance (detonation velocity 8.68 km·s$^{-1}$, detonation pressure 36.1 GPa), and low sensitivity, which can be employed as a melt-casting explosive [9]. In addition, Yi et al. prepared 3-(4-aminofurazan-3-yl)-4-(4-nitrofurazan-3-yl)furazan (ANTF, Scheme 1) from 3,4- bis(4′-aminofurazano-3′-yl)furazan precursor, and performance test revealed that ANTF is a potential melt-cast explosive with good thermal stability and detonation properties [10]. However, till now, most of investigated HEDMs based on furazan and furoxan backbone are negative oxygen balance, which could not supply enough oxygen for complete combustion, and thus their detonation energy is reduced to a certain extent.

In a continuing effort to screen out novel HEDMs with balanced detonation performance and sensitivity, in this work, we theoretically investigated three HEDMs in a combination of furazan and piperazine (Scheme 2), which could be synthesized by condensation, nitration and oxidation reactions. Here, the coupled heterocyclic backbone and zero

* Corresponding author.
*E-mail address:* helin201212@gmail.com (H. Lin).

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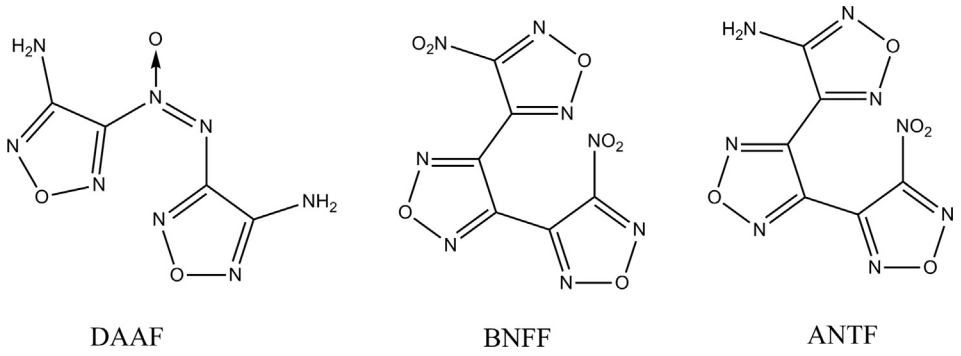
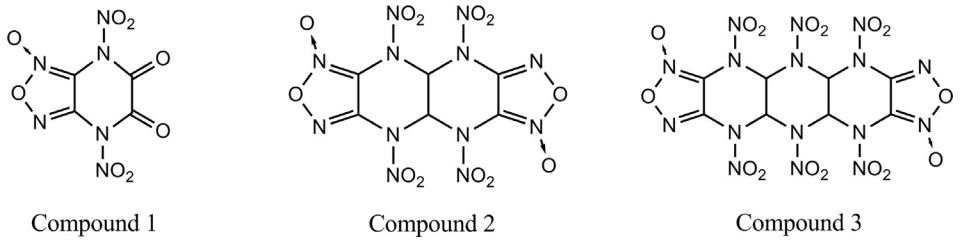



**Scheme 1.** Molecular structures of DAAF, BNFF, and ANTF.




**Scheme 2.** Molecular structures of three novel HEDMs.

oxygen balance were considered in our design strategy, because they could significantly enhance heats of formation and detonation performance of HEDMs. Our calculation results show that all these compounds have high densities, positive heats of formation, remarkable detonation performance and acceptable sensitivity. However, only compound 1 exhibits good thermal stability. Thus, compound 1 is the most attractive HEDM candidate.

## 2. Computational details

All density functional theory (DFT) calculations of this work were implemented in the Gaussian 09 programs [13]. Geometric structures of these three compounds were optimized using B3LYP method with 6–311 g(d,p) basis set, and they were determined to be true local energy minima on the potential energy surface via frequency analysis. Then, electronic structure and infrared spectrum were calculated at the same theory level.

To estimate the detonation performance of these three compounds, we calculated their heats of formation, heats of detonation, detonation velocities, and detonation pressures. Gas-phase heats of formation were obtained in terms of atom equivalent schemes [14], and solid-phase heats of formation were determined according to the Hess' law. Moreover, we employed the equation developed by Politzer et al. to predict their crystal densities [15]. Detonation velocity and detonation pressure as two critical parameters of HEDMs were evaluated using the empirical Kamlet-Jacobs equations [16].

Impact sensitivities ($H_{50}$) of these three compounds were calculated to evaluate their vulnerabilities to accidental explosion by the external impact, which could be expressed by the following 4 methods [17,18]:

$$\text{Method1: } H_{50} = -0.0064\sigma_+^2 + 241.42\nu - 3.43 \quad (1)$$

$$\text{Method2: } H_{50} = 9.2 + 8.03 \times 10^2 \times \exp[-0.3663 \times |\overline{V}^+ - |\overline{V}^-||] \quad (2)$$

$$\text{Method3: } H_{50} = 29.3 + 1.386 \times 10^{-3} \times \exp[48.84\nu] \quad (3)$$

$$\text{Method4: } H_{50} = 27.8 + 0.1135 \times \exp[-(11.0793 \times [Q_d - 1.6606])] \quad (4)$$

where $\sigma_+^2$ indicates the strength and variability of the positive surface potentials by the 0.002 au contour of electronic density, $|\overline{V}^+ - |\overline{V}^-||$describes the difference between the positive and negative surface potentials by the 0.001 au contour of electronic density, $\nu$ is the electrostatic balance parameter, and $Q_d$ is the heat of detonation.

The bond dissociation energy (BDE) was used to measure their thermal stability and calculated by:

$$BDE(A{-}B) = E_0(A) + E_0(B) - E_0(A{-}B) + \Delta E_{ZPE} \quad (5)$$

where $E_0(A)$, $E_0(B)$ and $E_0(A{-}B)$ are the energies of fragment A, fragment B and molecule A-B, respectively. $\Delta E_{ZPE}$ is the zero point energy difference between fragment A, fragment B and molecule A-B.

## 3. Results and discussion

To begin with, we initially explored structures of these three compounds. As shown in Fig. 1, their most stable configurations are composed of furazan and piperazine rings with abundant nitrogen and oxygen atoms. Each compound at least possesses two N-$NO_2$ bonds, which could dramatically improve their detonation energy. For compound 1, the furazan ring binds with piperazine ring in the same plane, and the average N-$NO_2$ bond length is 1.536 Å. While for compound 2 and 3, the furazan and piperazine rings are not coplane, and the N-$NO_2$ bond length becomes a little longer, due to large strain in the multicyclic systems.

After understanding the structural properties, we start to examine their electronic structures. Fig. 2 displays the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and their energy gap. Obviously, the HOMOs are dominated by the furazan ring, and the LUMOs are mainly contributed from the piperazine ring. In addition, all designed compounds exhibit large band gaps in the range of 3.84–4.16 eV. It is well-known that the kinetic stability and chemical reactivity of a molecule is closely related to its band gap [19]. Generally, a molecule with large band gap is chemically stable. In this regards, it could be concluded that all designed compounds have good stability in the chemical process, and their intramolecular charges could not be easily transferred from the electron donor to the electron acceptor.

To visualize their chemical reactivity sites, the electrostatic potentials (ESPs) were calculated at B3LYP/6-311G(d,p) level with isolevel of 0.001 electron/bohr$^3$, as shown in Fig. 3. The negative potential is denoted in red, and the positive one is denoted in blue. It is clear that the negative potentials are mostly distributed on the N-$NO_2$ bonds, and