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Computational studies on the heats of formation, energetic properties, and thermal stability of energetic nitrogen-rich furazano[3,4-b]pyrazine-based derivatives

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ABSTRACT

The heats of formation (HOF), energetic properties, and thermal stability for a series of furazano[3,4-b]pyrazine derivatives with different substituents or nitrogen-containing heterocycles were studied by using density functional theory. It is found that $-N_3$ or nitrogen-containing heterocycle is an effective structural unit for improving the HOF values of the derivatives. The calculated detonation velocities and detonation pressures indicate that the substitution of $-NO_2$, $-NF_2$, or NO_2-substituted heterocycle is very useful for enhancing their detonation performance. An analysis of the bond dissociation energies for several relatively weak bonds suggests that most of the derivatives have good thermal stability. By and large, the N–O bond in the furazano[3,4-b]pyrazine ring is the weakest one and the ring cleavage may happen in thermal decomposition. Considered the detonation performance and thermal stability, three compounds may be considered as the potential candidates of high energy density materials.

1. Introduction

Nitrogen-rich heterocyclic compounds have been investigated extensively to screen promising candidates for high-energy density materials (HEDMs) [1–5] owing to their rather high positive heat of formation (HOF), high densities, and good thermal stability. The furazano[3,4-b]pyrazine heterocyclic system has attracted considerable interest since its nitro derivatives were recommended for energetic applications in the middle of 1980s [6–8]. The furazano[3,4-b]pyrazine derivatives were synthesized first in 1969 [9]. Afterwards, much work has concentrated on the synthesis and properties of many furazano[3,4-b]pyrazine derivatives including its polycyclic derivatives and hydrogenated derivatives [10–18]. Although these studies provided profound insight into the chemistry and properties of furazano[3,4-b]pyrazine derivatives, there is still lacking comprehensive investigations on explosive performances and systematic molecular design for furazano[3,4-b]pyrazine-based compounds with higher performance and less sensitivity. To screen energetic compounds with high explosive performance, there is a clear need to continue to design and discover new furazano[3,4-b]pyrazine-based HEDMs.

In the past several decades, molecular designs based on quantum chemical treatment have gained acceptance as a useful research tool to screening promising high-energy density material. Theoretical studies can provide understanding in terms of the relationships between molecular structure and property and in turn can help design better and more efficient laboratory tests [19]. Therefore, the optimization of furazano[3,4-b]pyrazine-based molecules with high density and energy is the primary step for designing and synthesizing HEDMs.

It is well known that the introduction of the $-NO_2$ and $-NF_2$ group is helpful to enhance the explosive performances of an energetic material [5,20–25]. Also, a furazan, tetrazine, tetrazole, or triazole ring is a useful structural unit to design energetic materials since it has inherently high nitrogen content and good thermal stability [25–29]. At present, many theoretical studies pay more attention to designing new high-energy density compound by introducing different substituents such as $-NO_2$, $-NF_2$, and $-N_3$, but more and less ignore the effects of incorporating different nitrogen-containing heterocyclic rings.

In this work, we systematically investigated the heats of formation, energetic properties, and thermal stability of a series of furazano[3,4-b]pyrazine derivatives by using density functional theory (DFT) method. The HOFs of the substituted derivatives were calculated by designing isodesmic reactions. Next their detonation velocities and pressures were predicted using the calculated HOFs and densities. Then their thermal stabilities were evaluated based on their bond dissociation energies. It is expected that our results can provide useful information for the molecular design of novel HEDMs.

The remainder of this paper is organized as follows. A brief description of our computational method is given in Section 2.

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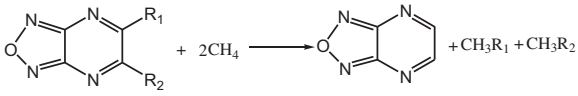
The results and discussion are presented in Section 3, followed by a summary of our conclusions in Section 4.

2. Computational method

The object molecules, a series of furazano[3,4-b]pyrazine derivatives (molecular numbering as A1–A6, B1–B6, C1–C6, D1–D6, E1–E6, F1–F6, G1–G6, H1–H6, and I1–I6), are classed into nine groups as shown in Fig. 1. The hybrid DFT-B3LYP methods with the 6-311G(d,p) basis set were adopted for structure optimizations of the molecular structures and the predictions of HOFs. Previous studies have shown that the basis set 6-311G(d,p) is able to predict the molecular structures and energies of energetic organic compounds [5,20,30,31].

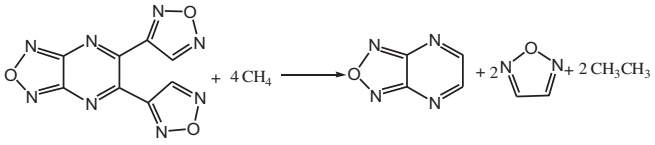
The method of isodesmic reactions was employed to calculate their HOFs using total energies obtained from the DFT-B3LYP/6-311G(d,p) calculations. Here we design isodesmic reactions in which the numbers of all kinds of bonds keep invariable to decrease the calculation errors of HOF. Because the electronic circumstances of reactants and products are very similar in isodesmic reactions, the errors of electronic correction energies can be counteracted, and then the errors of the calculated HOF can be greatly reduced. In our designed reactions, the basic structural unit of furazano[3,4-b]pyrazine skeleton and nitrogen-containing heterocycles skeleton remain invariable, and the big molecules are changed into small ones too. This approach has been demonstrated to predict reliably the HOFs of many organic systems [2,28,32,33].

The isodesmic reactions used to obtain the HOFs of the furazano[3,4-b]pyrazine derivatives at 298 K are as follows:



(1)

where R_1 or R_2 = –H, –NH_2, –NO_2, –ONO_2, –NF_2, –N_3, furazan, tetrazine, tetrazole, and triazole. If R_1 or R_2 contains the heterocyclic unit such as furazan, tetrazine, tetrazole, or triazole, the heterocyclic skeleton is also kept invariable. For example, if R_1 and R_2 are the furazan groups, the isodesmic reaction is as follows:

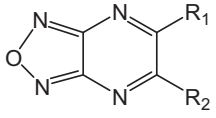


(2)

For the isodesmic reaction, the heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (3)$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively. As the experimental HOFs of CH_3NF_2, CH_3N_3, furazan, 1,2,4,5-tetrazine, 1,2,3-triazole, and furazano[3,4-b]pyrazine are unavailable, additional calculations were carried out for the atomization reaction: $C_aH_bN_c \rightarrow aC(g) + bH(g) + cN(g)$ at the G2 or CBS-Q level to get their HOFs. The G2 theory [34] and the complete basis set (CBS-Q) method [35,36] has been verified to be able to predict the HOFs accurately, but the G2 theory is more expensive and cannot calculate the total energies of some big molecules. The



A1 R_1=H R_2=-NH_2
A2 R_1=H R_2=-NO_2
A3 R_1=H R_2=-ONO_2
A4 R_1=H R_2=-NF_2
A5 R_1=H R_2=-N_3

B1 R_1=R_2=-NH_2
B2 R_1=R_2=-NO_2
B3 R_1=R_2=-ONO_2
B4 R_1=R_2=-NF_2
B5 R_1=R_2=-N_3

C1 R_1=-NO_2 R_2=-NH_2
C2 R_1=-NO_2 R_2=-ONO_2
C3 R_1=-NO_2 R_2=-NF_2
C4 R_1=-NO_2 R_2=-N_3

D1 R_1=H R_2=-furazan
D2 R_1=H R_2=-tetrazole(C)
D3 R_1=H R_2=-tetrazole(N)
D4 R_1=H R_2=-triazole
D5 R_1=H R_2=-tetrazine

E1 R_1=R_2=-furazan
E2 R_1=R_2=-tetrazole(C)
E3 R_1=R_2=-tetrazole(N)
E4 R_1=R_2=-triazole
E5 R_1=R_2=-tetrazine

F1 R_1=-NO_2 R_2=-furazan
F2 R_1=-NO_2 R_2=-tetrazole(C)
F3 R_1=-NO_2 R_2=-tetrazole(N)
F4 R_1=-NO_2 R_2=-triazole
F5 R_1=-NO_2 R_2=-tetrazine

G1 R_1=H R_2=-nitrofurazan
G2 R_1=H R_2=-nitrotetrazole(C)
G3 R_1=H R_2=-nitrotetrazole(N)
G4 R_1=H R_2=-nitrotriazole
G5 R_1=H R_2=-nitrotetrazine

H1 R_1=R_2=-nitrofurazan
H2 R_1=R_2=-nitrotetrazole(C)
H3 R_1=R_2=-nitrotetrazole(N)
H4 R_1=R_2=-nitrotriazole
H5 R_1=R_2=-nitrotetrazine

I1 R_1=-NO_2 R_2=-nitrofurazan
I2 R_1=-NO_2 R_2=-nitrotetrazole(C)
I3 R_1=-NO_2 R_2=-nitrotetrazole(N)
I4 R_1=-NO_2 R_2=-nitrotriazole
I5 R_1=-NO_2 R_2=-nitrotetrazine

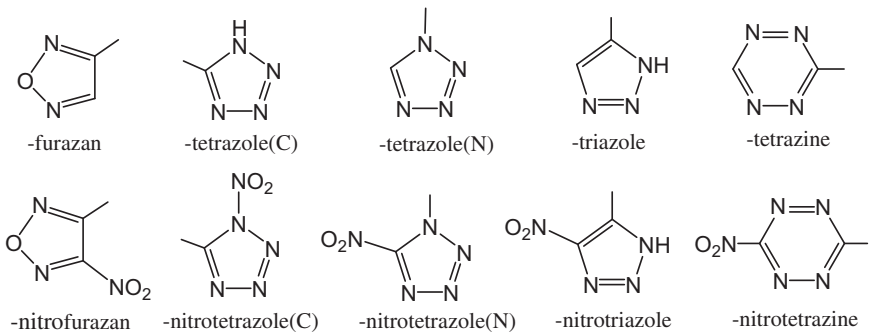


Fig. 1. Molecular frameworks of the furazano[3,4-b]pyrazine derivatives (molecular numbering as A1–A5, B1–B5, C1–C4, D1–D5, E1–E5, F1–F5, G1–G5, H1–H5, and I1–I5).