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Computational studies on thermodynamic properties, detonation properties and bond dissociation energies for polydifluoroaminopurine compounds

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ABSTRACT

Density functional theory (DFT) was used to study the heat of formation (HOFs), electronic structure, energetic properties and thermal stability for a series of purine derivatives with difluoroamino groups. The isodesmic reaction method was employed to calculate the HOFs of the energies obtained from electronic structure calculations. Results indicated that the position of difluoroamino groups could influence the values of HOFs. The bond dissociation energies and bond orders of the weakest bonds were analyzed to investigate the thermal stability of the purine derivatives. Furthermore, the detonation velocities and pressure were evaluated by using the Kamlet–Jacobs equations based on the theoretical densities and detonation heat (Q). The cylinder wall velocities ($\bar{V}$) were also calculated using the simplified calculational method. Compared with the conventional explosives, two purine derivatives may be regarded as the potential candidates for practical HEDCs.

1. Introduction

With the development of national defense and economy, more and more high energy density compounds (HEDCs) have been extensively studied as ingredients for explosives, fuels and propellant formulations [1–7]. Molecules, which possess the superior explosive performance, have been receiving highly heated attention because they may be substituted for traditional energetic compounds as HEDCs [8–12]. At present, a commonly used method of obtaining HEDCs is to add highly energetic groups as substitutes to a compound or polymer chain in order to increase the energetic character and improve oxygen balance, such as nitro, nitrate, nitramine groups and so on [13,14]. In support of computer technology and theoretical chemistry, computer modeling and quantum simulation have been extensively used to facilitate "molecular design". Nowadays, an increasing number of scientists throw themselves into "molecular design" to look for good HEDCs. Most research works are focused on high-nitrogen heterocyclic compounds and some important results have been achieved [15,16].

As everyone knows, heterocyclic nitramines constitute a class of organic energetic compounds and have played important roles in the civil and military fields for a long time. Typical examples of these well-known explosives are RDX (1,3,5-trinitro-1,3,5-triazinane) [17,18], HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) [19,20] and TNAZ (1,3,3-tirnitoazetidine). Recently, another type of organic nitamines compound, polydifluoroaminopurines, entered our line of sight. The basic structures and the atom numbering schemes used for the polydifluoroaminopurines are presented in Fig. 1. Purine received extremely widespread attention in biology because it is a mother frame for many important biologic compounds: guanine,

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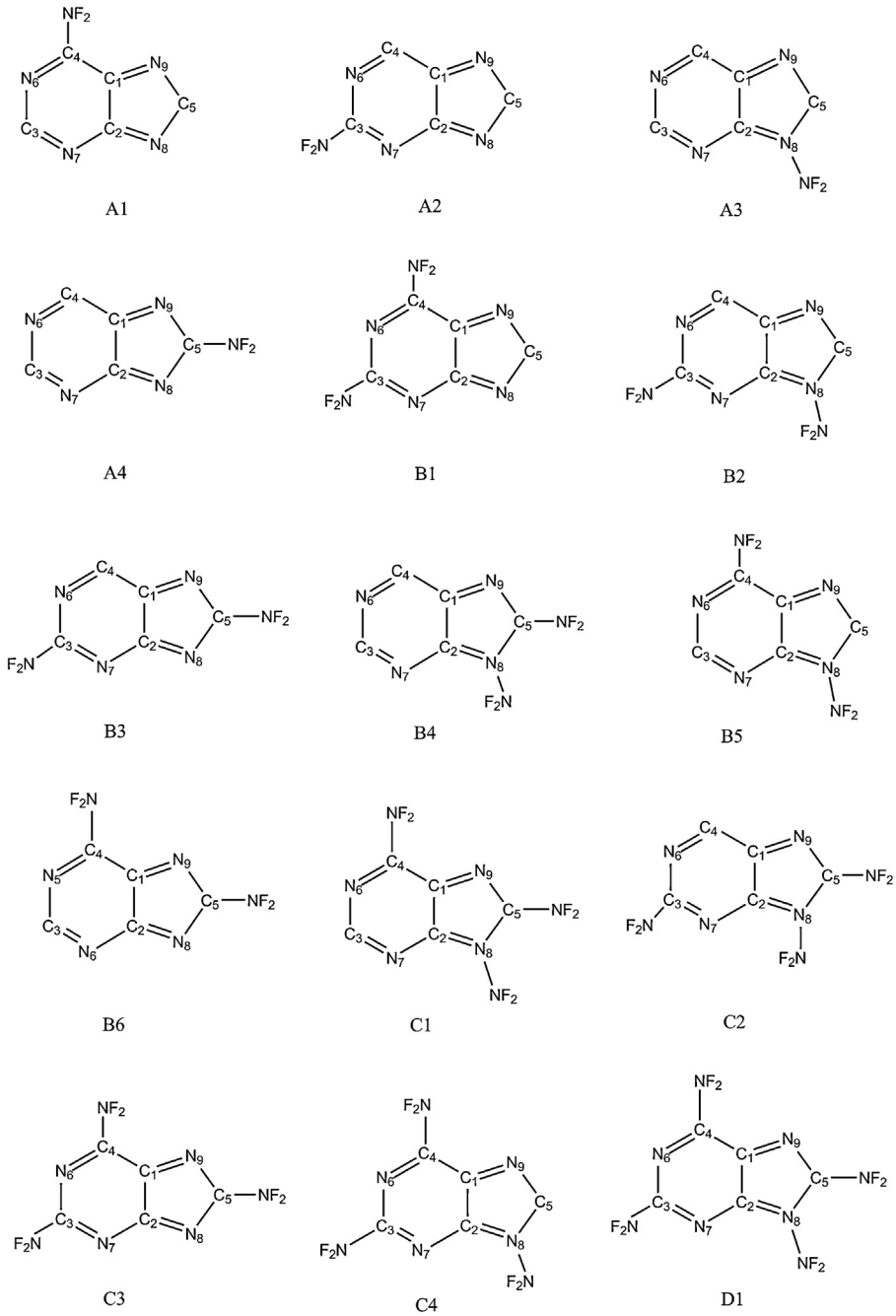

Fig. 1. Structures and atom numbering schemes used for the polydifluoroaminopurines.

xanthine adenine, hypoxanthine, theobromine and many others [21–23]. In addition, purine has a nitrogen content of more than 46%, and it is also fascinating because of four hydrogen atoms at the ring that can be replaced with functional groups. It is well known that the addition of energy-rich substituents, such as $-NO_2$, $-N_3$, $-NO_3$, and $-NNO_2$, create exceptionally powerful explosives, propellants, and fuels with excellent explosive properties. In the present work, we have conducted a systematic study on the basis of the purine structure modification in order to get satisfactory HEDCs. Compounds containing two fluorine atoms bonded to nitrogen, i.e., a difluoroamino (NF_2) group, have been extensively studied as ingredients for propellants and explosives [24–26]. When the difluoroamino groups are attached to the purine skeleton, ploydifluoroaminopurines are formed. In this article, 15 derivatives of purine are designed through substituting the hydrogen atoms in purine using difluoroamino groups, and the geometry, thermodynamic characters, and detonation performance are calculated in detail. These results provide