Molecular Design of 1,2,4,5-Tetrazine-Based High-Energy Density Materials

Tao Wei,[†,‡] Weihua Zhu,*[,†] Xiaowen Zhang,[†] Yu-Fang Li,[†] and Heming Xiao*[,†]

Institute for Computation in Molecular and Materials Science and Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China and Department of Pharmacy, Wenzhou Medical College, Wenzhou 325035, Zhejiang Province, China

Received: March 14, 2009; Revised Manuscript Received: July 9, 2009

The heats of formation (HOFs) for a series of 1,2,4,5-tetrazine derivatives were calculated by using density functional theory (DFT), Hartree Fork (HF), and Møller−Plesset (MP2) as well as semiempirical methods. The effects of different basis bets on HOFs were also considered. Our results show that the $-CN$ or $-N_3$ group plays a very important role in increasing the HOF values of the 1,2,4,5-tetrazine derivatives. An analysis of the bond dissociation energies for the weakest bonds indicates that substitutions of the $-N_3$, $-NH_2$, $-CN$, $-OH$, or $-Cl$ group are favorable for enhancing the thermal stability of 1,2,4,5-tetrazine, but the $-NHNH_2$, $-NHNO_2$, $-NO_2$, $-NF_2$, or $-COOH$ group produces opposite effects. The calculated detonation velocities and pressures indicate that the $-NF_2$ or $-NO_2$ group is very helpful for enhancing the detonation performance for the derivatives, but the case is quite the contrary for the $-CN$, $-NH_2$, or $-OH$ group. Considered the detonation performance and thermal stability, three derivatives may be regarded as potential candidates of high-energy density materials (HEDMs).

1. Introduction

High-energy density materials (HEDMs) have attracted considerable attention in recent years.[1−6] Energetic high-nitrogen organic compounds[7] are promising candidates for HEDMs and have become a hot research area owing to their novel properties including high density,[8,9] high positive heat of formation,[10,11] and high thermal stability.[12,13] 1,2,4,5-Tetrazine (or s-tetrazine) is an azo compound with an high nitrogen content (68.3%), making it of interest for the synthesis of highly energetic materials.[14] Much work[15−20] has concentrated on the synthesis and properties of many 1,2,4,5-tetrazine derivatives. Some of them have displayed potential as energetic additives for high explosive/rocket propellant formulations and pyrotechnic ingredients. Therefore, there is a clear need to continue to discover 1,2,4,5-tetrazine-based HEDMs.

The optimization of 1,2,4,5-tetrazine-based molecules with high density and energy is the primary step for designing and synthesizing HEDMs. Properties are often manipulated by making structural modifications. Theoretical studies can make it possible to screen candidate compounds, thereby avoiding expensive experimental tests. Also, they may provide understanding in terms of the relationships between molecular structure and property, which in turn can help design better and more efficient laboratory tests.

It is well known that evaluation of explosive performances of energetic materials requires knowledge of the heats of formation (HOFs). However, it is impractical or impossible to measure HOF for an energetic compound since there are many intermediates for energetic compounds. In these cases, it is of great importance to use computational methods that can accurately estimate HOFs. The parametrized semiempirical molecular orbital (MO) methods are able to figure out HOFs directly and rapidly.[21−24] Although these methods often bring significant HOFs errors for various groups and skeletons, the errors are sometimes systematic and can be corrected. Ab initio MO methods are employed to calculate HOF too. Energy is the most demanding quantity determined from computational studies. Unlike geometries, which in general can be produced in satisfactory agreement with the results using semiempirical methods and low-level ab initio calculations (Hartree−Fock, HF), high-level ab initio calculations are required to predict the energies accurately.[25] For comparison, very high-level methods which include expensive electron correlation with an extended basis set are required. To obtain accurate total energies, one often needs to perform high-level calculations such as quadratic configuration interaction with single and double excitations (QCISD) and Møller−Plesset (MP2) methods, which are computationally expensive and even impossible for large molecules. Nowadays, the density functional theory (DFT)[26,27] method including electron correlation not only produces reliable geometries and energies but also requires less time and computer resources. Consequently, it has become an important and economical tool to deal with complex systems and been widely employed.

In this work, we reported a systematic study on the HOFs, thermal stability, and energetic properties of a series of 1,2,4,5-tetrazine derivatives by using the DFT method. First, the HOFs of five 1,2,4,5-tetrazine derivatives (whose experimental values are available) were calculated using different methods via designed isodesmic reactions, and the reliability of methods was compared. Second, the HOFs of 17 1,2,4,5-tetrazine derivatives were predicted at the DFT-B3P86 level with the 6-311G** basis set. Then, their thermal stabilities were evaluated based on their bond dissociation energies. Finally, their detonation velocities and pressures were predicted using the calculations of HOFs and molecular volumes.

The remainder of this paper is organized as follows. A description of our computational method is given in section 2. The results and discussion are presented in section 3 followed by a summary of our conclusions in section 4.

---

* To whom correspondence should be addressed. E-mail: zhuwh@mail.njust.edu.cn; xiao@mail.njust.edu.cn.

[†] Nanjing University of Science and Technology.

[‡] Wenzhou Medical College.

10.1021/jp902295v CCC: $40.75

2. Computational Methods

The HF, MP2, hybrid DFT-B3LYP, and DFT-B3P86 methods with the 6-311G** basis set were adopted for the prediction of HOFs via designed isodesmic reactions.[28−35] The method of isodesmic reactions has been employed very successfully to calculate HOF from total energies obtained from ab initio calculations. The so-called isodesmic reaction processes, in which the number of each kind of formal bond is conserved, must comply with the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds.[33] However, usual bond separation reaction rules cannot be applied to the molecules with delocalized bonds and cage skeletons because of large calculated errors of HOFs. Therefore, we design isodesmic reactions in which the numbers of all kinds of bonds remain 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.[25] In these designed reactions, the basic structural unit of the 1,2,4,5-tetrazine ring skeleton remains invariable, and the big molecules are changed into small ones too. This approach has been proved to be reliable.[28−30] The object molecules are classed into four groups as shown in Figure 1.

The isodesmic reactions used to derive the HOFs of s-tetrazine derivatives at 298 K are as follows

$$\text{LAX-112} + 2H_2 + 2CH_4 \rightarrow \text{S} + 2CH_3NH_2 + 2H_2O \tag{1}$$

$$\text{ANAT} + 2CH_4 \rightarrow \text{S} + CH_3NH_2 + CH_3NHNO_2 \tag{2}$$

$$\text{S-2R} + 2CH_4 \rightarrow \text{S} + 2CH_3R \tag{3}$$

$$\text{S-R} + CH_4 \rightarrow \text{S} + CH_3R \tag{4}$$

where R = $-N_3$, $-NH_2$, $-NHNH_2$, $-NHNO_2$, $-CN$, $-NF_2$, $-NO_2$, $-OH$, $-Cl$, and $-COOH$. S is 1,2,4,5-tetrazine. For the isodesmic reactions 1−4, the heat of reaction (ΔH_{298}) at 298 K can be calculated from the following equation

$$\Delta H_{298K} = \sum \Delta H_{f,p} - \sum \Delta H_{f,R} \tag{5}$$

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, CH_3NHNO_2, and 1,2,4,5-tetrazine are unavailable, additional calculations were carried out for the replacement reaction $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$ using G2 theory to get an accurate value of ΔH_f for CH_3NF_2.[31] The HOF value of CH_3N_3 was carried out at the G2 level from the atomization reaction: $CH_3N_3 \rightarrow C(g) + 3H(g) + 3N\ (g)$.[35] The value of 1,2,4,5- tetrazine was carried out at the G2 level[36,37] from the atomization reaction $C_2H_2N_4 \rightarrow 2C + 2H + 4N$ and the isodesmic reaction $CH_3NHNO_2(g) + CH_4(g) \rightarrow CH_3NH_2(g) + CH_3NO_2(g)$. The experimental HOFs of reference compounds CH_4, CH_3NH_2, H_2, H_2O, CH_3NHNH_2, CH_3CN, CH_3NO_2, CH_3OH, CH_3COOH, and CH_3Cl are available. The HOFs of 1,2,4,5-tetrazine derivatives can be figured out when the heat of reaction ΔH_{298} is known. Therefore, the most important thing is to compute the ΔH_{298}. ΔH_{298} can be calculated using the following expression

$$\Delta H = \Delta E_{298K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \tag{6}$$

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 (ZPE) of the products and the reactants, and ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq 6 is the PV work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions 1−4, $\Delta n = 0$, so $\Delta(PV) = 0$.

The strength of bonding, which could be evaluated by the bond dissociation energy, is fundamental to understanding chemical processes.[38] The energy required for homolytic bond cleavage at 298 K and 1 atm corresponds to the enthalpy of reaction 7, $\Delta_{rxn}H_{298}(7)$, which is by definition[39] the bond dissociation enthalpy of the molecule A−B, $\Delta H_{298}(A-B)$

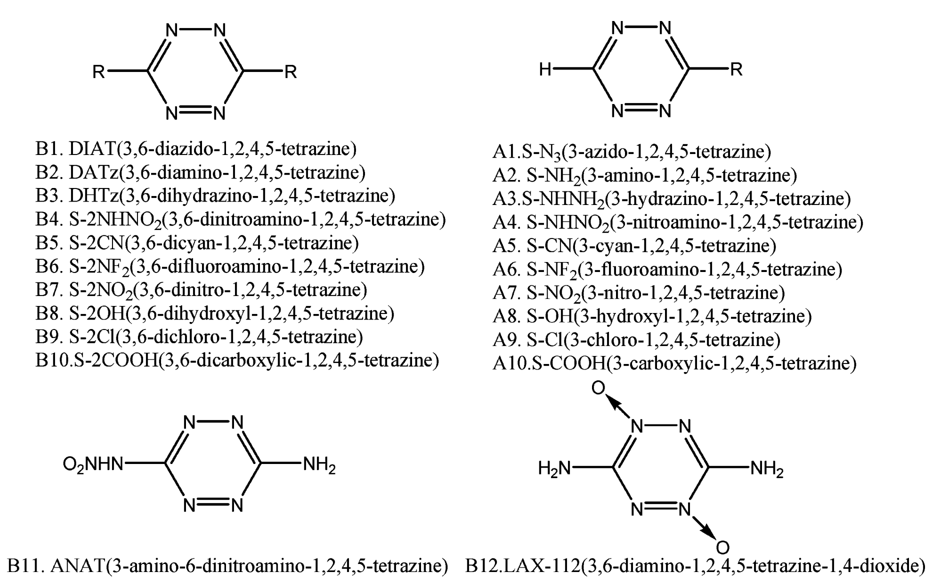

Figure 1. Molecular frameworks of 1,2,4,5-tetrazine derivatives.

$$A{-}B(g) \rightarrow A{\bullet}(g) + B{\bullet}(g) \qquad (7)$$

By definition, it is the reaction enthalpy of the bond homolysis reaction 7, $\Delta_f H_{298}7$, and thus depends exclusively on the relative enthalpies of formation of reactant and product states[40]

$$\Delta_{rxn}H_{298}(7) = \Delta_f H_{298}(A\bullet) + \Delta_f H_{298}(B\bullet) - \Delta_f H_{298}(A{-}B) = \Delta H_{298}(A{-}B) \qquad (8)$$

where $\Delta_f H_{298}(A\bullet)$ and $\Delta_f H_{298}(B\bullet)$ are the enthalpies of formation of the radicals and $\Delta_f H_{298}(A{-}B)$ is the enthalpy of formation of the molecule.

For many organics, $BDE^0(A{-}B)$ and $\Delta H_{298}(A{-}B)$ are almost numerically equivalent, and as a consequence, the terms "bond dissociation energy" (BDE) and "bond dissociation enthalpy" often appear interchangeably in the literature.[40] Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of eq 9[40]

$$BDE^0(A{-}B) = E_0(A\bullet) + E_0(B\bullet) - E_0(A{-}B) \qquad (9)$$

The bond dissociation energy with zero-point energy (ZPE) correction can be calculated by eq 10

$$BDE(A{-}B)_{ZPE} = BDE^0(A{-}B) + \Delta ZPE \qquad (10)$$

where ΔZPE is the difference of the ZPEs of the products and the reactants.

The calculations were performed with the Gaussian 98 package[41] at the DFT-B3LYP, DFT-B3P86, HF, MP2, and G2 levels as well as at the AM1 and PM3 levels. The optimizations were performed without any symmetry restrictions using the default convergence criteria in the programs. All of the optimized structures were characterized to be true local energy minima on the potential-energy surfaces without imaginary frequencies.

The detonation velocity and pressure were estimated by the empirical Kamlet−Jacobs formula[42] as

$$P = 1.558^2_{\rho}\varphi \qquad (11)$$

$$D = (1.011 + 1.312_{\rho})\varphi^{1/2} \qquad (12)$$

where P is the predicted detonation pressure in GPa, D is the detonation velocity in km/s, ρ is the density of a compound in g/cm^3, and φ is a characteristic value related to both the HOF and the molecular stoichiometry of an explosive. The density of a compound needs the datum of the molecular volume. The volume was defined as inside a contour of 0.001 electrons/Bohr^3 density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for each optimized structure to get an average volume at the B3LYP/6-31G* level. This method has been successfully applied to various CHNO molecules.[43]

3. Results and Discussion

3.1. Heats of Formation. The HOF is frequently taken to be indicative of the "energy content" of a HEDM. Therefore, it is very important to accurately predict the HOF. In this section, we investigate the computational parameters on the HOFs as a base for studying other molecules and as a well-studied benchmark. Figure 1 shows the molecular frameworks of a series of 1,2,4,5-tetrazine derivatives (single substituent and double substituents). The experimental HOFs of the reference compounds (including CH_4, CH_3NH_2, CH_3NHNH_2, H_2, H_2O, CH_3CN, CH_3NO_2, CH_3OH, CH_3COOH, and CH_3Cl) in the isodesmic reactions 1−4 were taken from refs 29, 44, and 45. Accurate values of ΔH_f for CH_3NF_2 and CH_3N_3 were obtained from refs 31 and 35, respectively. The heat of atomization reaction, ΔH_{298}, for the reaction $S(g) \rightarrow 2C(g) + 2H(g) + 4N(g)$ and the heat of isodesmic reaction, ΔH_{298}, for the reaction $CH_3NHNO_2(g) + CH_4(g) \rightarrow CH_3NH_2(g) + CH_3NO_2(g)$ were obtained through eq 6 using the G2 theory.[36,37] An accurate value of ΔH_f for 1,2,4,5-tetrazine and CH_3NHNO_2 were then obtained through eq 5 as well as the available experimental HOFs for C(g), H(g), N(g), $NH_3(g)$, $CH_4(g)$, CH_3NO_2, and $NH_2NO_2(g)$. There are no experimental HOFs values of 1,2,4,5-tetrazine and CH_3NHNO_2 for comparison. To validate the reliability of our results, we only compare the calculated ΔH_f values of triazole and NH_2NO_2 at the G2 level with their experimental data. The ΔH_f value of triazole is calculated by the G2 theory to be 193.52 kJ/mol, very close to the experimental ΔH_f of 193.70 kJ/mol[46] with an error of only 0.18 kJ/mol. Also, the ΔH_f value of NH_2NO_2 is obtained at the G2 level from the isodesmic reaction $NH_2NO_2(g) + CH_4(g) \rightarrow NH_3(g) + CH_3NO_2$ to be −3.2 kJ/mol, fully consistent with the experimental ΔH_f of −3.2 kJ/mol.[29] Therefore, the HOF values from the G2 theory are expected to be reliable for 1,2,4,5-tetrazine and CH_3NHNO_2 since 1,2,4,5-tetrazine and triazole have similar structural characters as well as CH_3NHNO_2 and NH_2NO_2. In addition, we obtained the ΔH_f of −3.73 kJ/mol for NH_2NO_2 at the G2 level via the atomization reaction $NH_2NO_2(g) \rightarrow 2H(g) + 2N(g) + 2O(g)$ with an error of 0.53 kJ/mol. This indicates that the isodesmic reaction is slightly better than the atomization reaction for calculating the ΔH_f of NH_2NO_2.

3.1.1. Choice of Basis Sets. First, the total energies, zero-point energies, and thermal corrections for the title compounds were calculated, and then the HOF values were obtained using eq 6. Table 1 lists the calculated HOFs of five 1,2,4,5-tetrazine derivatives at the DFT-B3LYP level with various basis sets as well as available experimental values. Obviously, there are few discrepancies between different calculated results with different basis sets. The calculated HOFs are slightly larger than the experimental values via designed isodesmic reactions, especially for B2 and B3. This is because the experimental values were measured in the solid state, except the HOFs of B1 and B11 are the theoretical values,[18,48] while our calculations were performed in the gas phase. When the basis sets with diffuse functions are used, the calculated HOFs of five compounds are larger than the results by the basis sets without diffuse functions. However, the additions of the polarized functions slightly decrease the HOF values except for B12. It is interesting to note that the basis set 6-311G** produces relatively satisfactory results compared with the experiment values. Previous studies[25] have also reported that the standard 6-311G** basis set has been proven to be large enough to produce reliable results for organic compounds containing H, C, O, and N. Therefore, the 6-311G** basis set was used in all subsequent calculations.

3.1.2. Comparison of Different Methods. Table 2 lists the total energies, zero-point energies, thermal corrections, and HOFs for eight reference compounds in the isodesmic reactions 1−3 at the B3LYP/6-311G** and B3P86/6-311G** levels. Table 3 presents the results at the HF and MP2 levels with the

TABLE 1: Calculated Heats of Formation (HOF, kJ/mol) of the 1,2,4,5-Tetrazine Derivatives Using the Hybrid DFT-B3LYP Method

no.	compd	6-31G*	6-311G*	6-31+G*	6-31G**	6-311G**	6-31+G**	6-311++G**	expt
B1	DIAT	1126.47	1126.68	1130.94	1125.05	1125.05	1131.71	1133.31	1101[16]
B2	DATz	400.28	395.42	407.46	397.66	394.22	404.70	406.32	307[16]
B3	DHTz	625.22	650.32	662.47	621.98	649.24	660.34	662.47	536[19]
B11	ANAT	473.32	470.67	483.27	471.19	469.81	481.14	481.62	441[48]
B12	LAX-112	183.23	184.08	234.29	218.91	237.44	273.68	286.30	164[18]

TABLE 2: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the Reference Compounds at the B3P86 and B3LYP Levels[a]

	B3P86/6-311G**			B3LYP/6-311G**			
compd	E_0	ZPE	H_T	E_0	ZPE	H_T	HOF
S	−297.134547	135.414	13.87	−296.390906	134.40	13.84	481.60[b]
H_2	−1.215152	26.42	0.00	−1.179571	26.43	0.00	0.00
CH_4	−40.713980	117.42	10.04	−40.533744	117.09	10.03	−74.40[29]
H_2O	−76.625255	56.43	9.93	−76.447448	55.94	9.93	−241.80[44]
CH_3N_3	−204.679787	132.53	14.40	−204.148401	131.67	14.41	296.54[35]
CH_3NH_2	−96.213717	168.31	11.55	−95.888439	167.56	11.56	−23.01[29]
CH_3NHNH_2	−151.692042	214.55	13.70	−151.222209	213.43	13.74	94.35[45]
CH_3NHNO_2	−301.147794	177.78	16.30	−300.434462	176.49	16.34	−15.20[b]

[a] E_0 is in au; ZPE, HOF, and H_T are in kJ/mol. The scaling factor for ZPE is 0.98, and the scaling for H_T is 0.96.[49] [b] The calculated values are at the G2 level from the atomization reaction: $S(g) \rightarrow 2C(g) + 2H(g) + 4N(g)$, $CH_3NHNO_2(g) + CH_4(g) \rightarrow CH_3NH_2(g) + CH_3NO_2(g)$.

TABLE 3: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the Reference Compounds at the HF and MP2 Levels

	HF/6-311G**			MP2/6-311G**			
compd	E_0	ZPE	H_T	E_0	ZPE	H_T	HOF
S	−294.657559	147.34	13.27	−295.599734	134.99	13.99	481.60[a]
H_2	−1.132491	27.48	0.00	−1.160272	27.11	0.00	0.00
CH_4	−40.209012	123.26	10.03	−40.379234	119.43	10.04	−74.40[29]
H_2O	−76.047012	60.58	9.93	−76.263972	57.33	9.93	−241.80[44]
CH_3N_3	−202.918322	140.93	14.26	−203.599914	134.15	14.41	296.54[35]
CH_3NH_2	−95.242514	178.73	11.57	−95.587460	171.22	11.49	−23.01[29]
CH_3NHNH_2	−150.250325	229.71	13.70	−150.772259	218.27	13.65	94.35[45]
CH_3NHNO_2	−298.754900	191.88	16.04	−299.666475	181.06	16.08	−15.20[a]

[a] The calculated values are at the G2 level from the atomization reaction: $S(g) \rightarrow 2C(g) + 2H(g) + 4N(g)$, $CH_3NHNO_2(g) + CH_4(g) \rightarrow CH_3NH_2(g) + CH_3NO_2(g)$.

TABLE 4: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the 1,2,4,5-Tetrazine Derivatives at the B3P86 and B3LYP Levels[a]

		B3P86/6-311G**				B3LYP/6-311G**				
no.	compd	E_0	ZPE	H_T	HOF	E_0	ZPE	H_T	HOF	HOF
B1	DIAT	−625.102166	152.25	27.31	1120.56	−623.654470	149.96	27.42	1125.05	1101[16]
B2	DATZ	−408.206181	224.87	20.86	386.83	−407.169695	223.16	20.89	394.22	307[16]
B3	DHTZ	−519.156601	315.57	28.73	639.72	−517.830183	313.26	28.63	649.24	536[19]
B11	ANAT	−613.113062	231.35	27.36	464.85	−611.689380	228.78	27.54	469.81	441[48]
B12	LAX-112	−558.884704	248.19	25.32	223.85	−557.561574	245.85	25.43	237.44	164[18]

[a] E_0 is in au; ZPE, HOF, and H_T are in kJ/mol. The scaling factor for ZPE is 0.98, and the scaling for H_T is 0.96.[49]

6-311G** basis set. Thermodynamic properties were obtained from the vibrational frequencies scaled with scaling factors taken from Scott and Radom.[49] Tables 4 and 5 summarize the total energies, zero-point energies, thermal corrections, and HOFs for five 1,2,4,5-tetrazine derivatives. As is evident in Tables 4 and 5, all five compounds have positive HOFs. B1 has the largest HOF values among the derivatives and is over 1000 kJ/mol. This indicates that the 1,2,4,5-tetrazine derivatives have high positive HOFs, consistent with previous reports.[10,11] Although the calculated HOFs of five 1,2,4,5-tetrazine derivatives were larger than the experimental values, especially at the HF/6-311G** level, DFT and MP2 methods produce relatively satisfactory results, especially DFT-B3P86, compared with the experimental results.

We also evaluate the dependence of the HOFs on different methods. The results show that the HOFs at the B3P86, B3LYP, HF, and MP2 levels with 6-311G** for the same compound are very close to each other except at the HF level. There are very good linear relationships between the HOFs from B3P86 and B3LYP, MP2, or HF methods with 6-311G**: $HOF_{B3P86} = 1.007HOF_{B3LYP} - 12.034$ with $R = 0.9999$; $HOF_{B3P86} = 1.0512HOF_{MP2} - 42.414$ with $R = 0.9976$; $HOF_{B3P86} = 1.1492HOF_{HF} - 175.01$ with $R = 0.9442$.

Semiempirical MO methods could predict the HOFs directly and rapidly for a series of compounds. However, their validity is sometimes limited. Table 6 presents the HOFs of five 1,2,4,5-tetrazine derivatives at the AM1 and PM3 levels. It is found that the HOFs obtained from AM1 are larger than those from

TABLE 5: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the 1,2,4,5-Tetrazine Derivatives at the HF and MP2 Levels

		HF/6-311G**				MP2/6-311G**				
no.	compd	E_0	ZPE	H_T	HOF	E_0	ZPE	H_T	HOF	HOF
B1	DIAT	−620.106148	165.89	26.79	1134.53	−622.080187	149.89	28.08	1112.15	1101[16]
B2	DATZ	−404.777060	240.65	20.91	433.84	−406.085005	226.65	20.79	396.10	307[16]
B3	DHTZ	−514.785224	341.08	27.72	689.19	−516.448329	318.46	28.41	648.38	536[19]
B11	ANAT	−608.264886	250.86	27.19	506.43	−610.139707	233.02	27.1	465.89	441[48]
B12	LAX-112	−554.388192	265.69	25.04	465.12	−556.134562	251.88	25.45	277.04	164[18]

TABLE 6: Calculated Heats of Formation (HOF, kJ/mol) of the 1,2,4,5-Tetrazine Derivatives by Two Semiempirical MO Methods

no.	compd	AM1	PM3	HOF
B1	DIAT	1154.92	1014.27	1101[16]
B2	DATz	416.50	345.25	307[16]
B3	DHTz	626.13	567.67	536[19]
B11	ANAT	551.72	415.01	441[48]
B12	LAX-112	584.24	389.35	164[18]

PM3 and DFT. The HOFs by PM3 are closer to the experimental values than those by AM1. For LAX-112, the HOF values at the AM1 and PM3 levels are by far larger than the experimental results. Therefore, PM3 are more suitable for computing the HOFs of the 1,2,4,5-tetrazine derivatives.

Previous studies[28−31] have shown that the theoretically predicted values of HOFs were in good agreement with experiments when the appropriate reference compounds in the isodesmic reaction were chosen. An efficient way of reducing errors of HOFs is to keep the conjugated bonds unbroken. This approach has been proved to be reliable.[47] By comparison of different methods, the calculated HOFs of five title compounds are basically in accord with the experimental observations at the B3P86/6-311G** level. Therefore, the B3P86/6-311G** method is employed in the following calculations.

3.1.3. Prediction of HOFs. Table 7 lists the total energies, zero-point energies, thermal corrections, and HOFs for nine reference compounds in the isodesmic reactions 3 and 4 at the B3P86/6-311G** level. Table 8 summarizes the total energies, zero-point energies, thermal corrections, and HOFs for the 1,2,4,5-tetrazine derivatives. When the substituent is $-N_3$, $-NHNH_2$, $-NHNO_2$, $-CN$, or $-NO_2$, an increase in the HOF value of its substituted 1,2,4,5-tetrazine is large compared with the unsubstituted case. For the substituent $-NH_2$, $-NF_2$, $-OH$, $-Cl$ or $-COOH$, the case is quite the contrary. When the H atom of 1,2,4,5-tetrazine is replaced by $-N_3$, its HOF value is the largest one among these derivatives with the same number of substituents. It is seen in Table 8 that substitution of the group $-CN$ or $-N_3$ extremely enhances its HOF value compared to parent 1,2,4,5-tetrazine. This shows that the $-CN$ or $-N_3$ group plays a very important role in increasing the HOF values of the 1,2,4,5-tetrazine derivatives. We also note that the HOFs of the 1,2,4,5-tetrazine derivatives are not satisfactory with the relationship of simple group addition.

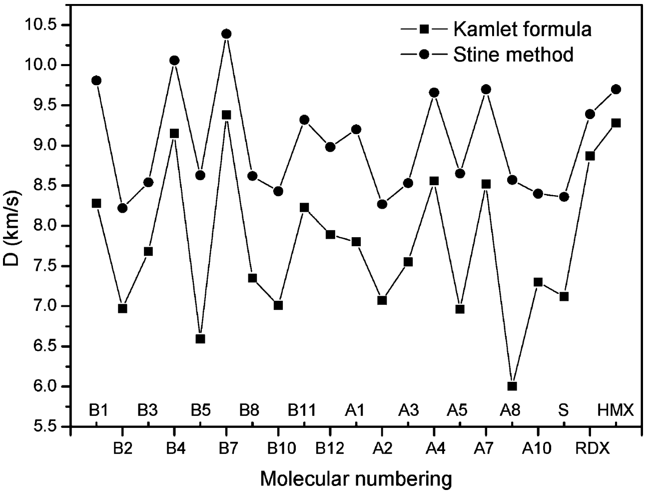

Figure 2. Comparison of the detonation velocities of the substituted 1,2,4,5-tetrazine obtained from the Kamlet−Jacobs formula with those from the Stine method.

3.2. Electronic Structure and Thermal Stability. Table 9 lists the HOMO and LUMO energies and the energy gaps ($\Delta E_{LUMO-HOMO}$) for the 1,2,4,5-tetrazine derivatives at the B3LYP/6-311G** and B3P86/6-311G** levels. It can be seen that the E_{HOMO} and E_{LUMO} values at the B3P86/6-311G** level are systematically smaller than those at the B3LYP/6-311G** level. The same is true of $\Delta E_{LUMO-HOMO}$ at the two levels. The variations of $\Delta E_{LUMO-HOMO}$ are very similar at the two levels. There is a good linear relationship between $\Delta E_{LUMO-HOMO}$ by B3LYP and $\Delta E_{LUMO-HOMO}$ by B3P86 with the 6-311G** basis set: $\Delta E_{B3LYP} = 1.1158\Delta E_{B3P86} - 0.0142$ with $R = 0.9947$. This shows that both methods produce similar energy gaps for the 1,2,4,5-tetrazine derivatives. When a $-NH_2$ or $-NHNH_2$ group is attached to the ring, the HOMO energy level increases, whereas attachment of other groups such as $-N_3$, $-NHNO_2$, $-CN$, $-NF_2$, $-NO_2$, $-Cl$, or $-COOH$ will make the HOMO energy level decrease. The same is true of the LUMO energy level for these derivatives. However, most of the derivatives increase the HOMO−LUMO gap as compared to the parent 1,2,4,5-tetrazine. B2, B4−9, B11, and A2−9 have higher energy gaps than the unsubstituted molecule, indicating a shift toward higher frequencies in their electronic absorption spectra. However, B1, B3, B10, B12, A1, and A10 have lower energy gaps than the unsubstituted one, reflecting a shift toward lower frequencies in their electronic absorption spectra. Among these derivatives, B7 has the highest ΔE value, whereas B12 has the smallest one. Overall, different substituted molecules present a comparison of the energetics.

Bond order is a measure of the overall bond strength between two atoms. A high value of the bond order indicates a covalent bond, while a low value shows an ionic nature. Table 10 presents the bond overlap populations of the C−N, N−N, C−R (R = $-N_3$, $-NH_2$, $-NHNH_2$, $-NHNO_2$, $-CN$, $-NF_2$, $-NO_2$, $-OH$, $-Cl$, $-COOH$), and N−R′ (R′ = $-NH_2$, $-NO_2$, $-O$, $-N_2$) bonds for the 1,2,4,5-tetrazine derivatives. It is found that the bond overlap populations on the C−R or N−R′ bonds are much smaller than those of the C−N and N−N bonds except for B2 and B8, whose populations of the $C-NH_2$ and C−OH bonds are larger than those of the N−N bonds. For B5−7 and B9−10, the C−R bond has the lowest bond order among all the bonds. This indicates that the trigger linkage in the compounds appears to be C−R homolysis, while other bonds are relatively strong and resistant to rupture. For the B1, B3, B4, B11, and B12

TABLE 7: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the Reference Compounds[a]

	B3P86/6-311G**					B3P86/6-311G**			
compd	E_0	ZPE	H_T	HOF	compd	E_0	ZPE	H_T	HOF
S	−297.134547	135.414	13.87	481.60[b]	CH_3NO_2	−245.649164	131.34	14.12	−80.80[44]
CH_4	−40.713980	117.42	10.04	−74.40[29]	CH_3OH	−116.078900	134.92	11.25	−432.20[44]
CH_3NHNO_2	−301.147794	177.78	16.3	−15.20[b]	CH_3COOH	−229.724376	162.68	14.68	201.50[29]
CH_3CN	−133.179776	119.05	12.06	79.50[29]	CH_3Cl	−500.635574	99.27	10.47	−81.90[29]
CH_3NF_2	−294.895029	123.62	13.75	−115.23[35]					

[a] E_0 is in au; ZPE, HOF, and H_T are in kJ/mol. The scaling factor for ZPE is 0.98, and the scaling for H_T is 0.96.[49] [b] The calculated values are at the G2 level from the atomization reaction: S(g) → 2C(g) + 2H(g) + 4N(g), CH_3NHNO_2(g) + CH_4(g) → CH_3NH_2(g) + CH_3NO_2(g).

TABLE 8: Calculated Total Energies (E_0, au), Zero-Point Energies (ZPE, kJ/mol), Thermal Corrections (H_T, kJ/mol), and Heats of Formation (HOF, kJ/mol) of the 1,2,4,5-Tetrazine Derivatives

	B3P86/6-311G**					B3P86/6-311G**			
compd	E_0	ZPE	H_T	HOF	compd	E_0	ZPE	H_T	HOF
B1	−625.102166	152.25	27.31	1120.56	A1	−461.119537	144.07	20.42	798.04
B2	−408.206181	224.87	20.86	386.83	A2	−352.674868	178.94	18.44	422.28
B3	−519.156601	315.57	28.73	639.72	A3	−408.150468	225.89	21.27	548.17
B4	−818.010901	237.98	33.22	566.13	A4	−557.573403	186.90	23.41	522.15
B5	−482.041920	125.13	23.28	845.08	A5	−389.589615	130.43	18.49	659.78
B6	−805.473690	129.89	28.88	450.23	A6	−551.305287	132.80	21.22	462.84
B7	−706.975989	146.34	27.74	533.88	A7	−502.057738	141.18	20.61	501.35
B8	−447.930996	161.51	18.62	46.13	A8	−372.535319	148.92	16.07	257.45
B9	−1216.977830	83.66	19.53	456.00	A9	−757.057060	109.62	16.6	466.49
B10	−675.140773	211.91	29.67	−202.98	A10	−486.138026	173.89	21.61	138.41
B11	−613.113062	231.35	27.36	464.85	S[a]	−297.134547	135.414	13.87	481.60
B12	−558.884704	248.19	25.32	223.85					

[a] S stands for 1,2,4,5-tetrazine.

TABLE 9: Calculated HOMO and LUMO Energies (au) and Energy Gaps ($\Delta E_{LUMO-HOMO}$) of the 1,2,4,5-Tetrazine Derivatives at the B3LYP/6-311G and B3P86/6-311G** Levels[a]**

compd	E_{HOMO}	E_{LUMO}	$\Delta E_{LUMO-HOMO}$
B1	−0.2655(−0.2872)	−0.1323(−0.1552)	0.1332(0.1320)
B2	−0.2297(−0.2506)	−0.0940(−0.1156)	0.1357(0.1350)
B3	−0.2260(−0.2472)	−0.1022(−0.1239)	0.1238(0.1233)
B4	−0.2816(−0.3029)	−0.1454(−0.1673)	0.1362(0.1356)
B5	−0.3031(−0.3249)	−0.1690(−0.1921)	0.1341(0.1328)
B6	−0.2977(−0.3177)	−0.1623(−0.1835)	0.1354(0.1342)
B7	−0.3199(−0.3409)	−0.1825(−0.2048)	0.1374(0.1361)
B8	−0.2579(−0.2780)	−0.1226(−0.1443)	0.1353(0.1337)
B9	−0.2823(−0.3021)	−0.1475(−0.1688)	0.1348(0.1333)
B10	−0.2840(−0.2885)	−0.1522(−0.1593)	0.1318(0.1293)
B11	−0.2556(−0.2767)	−0.1192(−0.1412)	0.1364(0.1355)
B12	−0.2120(−0.2341)	−0.0999(−0.1201)	0.1121(0.1140)
A1	−0.2595(−0.2808)	−0.1261(−0.1487)	0.1334(0.1320)
A2	−0.2370(−0.2576)	−0.1020(−0.1240)	0.1349(0.1336)
A3	−0.2403(−0.2612)	−0.1058(−0.1280)	0.1345(0.1332)
A4	−0.2684(−0.2893)	−0.1343(−0.1564)	0.1341(0.1329)
A5	−0.2808(−0.3022)	−0.1471(−0.1698)	0.1338(0.1325)
A6	−0.2775(−0.2978)	−0.1433(−0.1649)	0.1342(0.1329)
A7	−0.2895(−0.3104)	−0.1540(−0.1762)	0.1355(0.1342)
A8	−0.2556(−0.2763)	−0.1210(−0.1431)	0.1346(0.1332)
A9	−0.2699(−0.2902)	−0.1357(−0.1574)	0.1342(0.1328)
A10	−0.2621(−0.2831)	−0.1301(−0.1524)	0.1320(0.1306)
S[b]	−0.2554(−0.2762)	−0.1219(−0.1442)	0.1335(0.1320)

[a] The values in parentheses are at the B3P86/6-311G** level. [b] S stands for 1,2,4,5-tetrazine.

TABLE 10: Calculated Bond Overlap Populations of Part Bonds of the 1,2,4,5-Tetrazine Derivatives at the B3LYP/6-311G Level**

compd	P_{C-N}	P_{N-N}	$P_{C\text{-}R}$	$P_{N\text{-}R'}$
B1	0.4619	0.2919	0.3996	0.2161 (P_{N-N2})
B2	0.4871	0.3322	0.3738	
B3	0.4763	0.3295	0.3478	0.2712 ($P_{NH\text{-}NH2}$)
B4	0.4580	0.3175	0.2738	0.1699 ($P_{NH\text{-}NO2}$)
B5	0.4567	0.3197	0.1137	
B6	0.4454	0.2836	0.2191	
B7	0.4418	0.2859	0.1471	
B8	0.4635	0.2861	0.3796	
B9	0.4301	0.2978	0.2611	
B10	0.4090	0.2911	0.1076	
B11	0.4170	0.2734	0.3944	0.2365 (P_{N-O})
B12	0.4719	0.3279	0.3331	0.1779 (P_{NH-NO2})
A1	0.4630	0.2924	0.3926	0.2094 (P_{N-N2})
A2	0.4757	0.3194	0.3766	
A3	0.4691	0.3158	0.3519	0.2603 (P_{NH-NH2})
A4	0.4619	0.3035	0.2648	0.1656 (P_{NH-NO2})
A5	0.4651	0.3009	0.1107	
A6	0.4634	0.2871	0.2149	
A7	0.4608	0.2865	0.1471	
A8	0.4602	0.2883	0.3827	
A9	0.4548	0.2901	0.2574	
A10	0.4566	0.2861	0.1314	
S[a]	0.4676	0.2835		

[a] S stands for 1,2,4,5-tetrazine.

compounds, the N−R′ bond has the lowest population, so their fragmentation pathways may concern the R′ radical. However, the case is quite the contrary for B2 and B8, whose N−N bond has the weakest population, showing ring cleavage is possible to happen in thermal decomposition. It is interesting to note that all the derivatives have higher bond orders of the N−N bonds than 1,2,4,5-tetrazine, whereas only B2−3, A2−3, and B12 derivatives increase the bond orders of the C−N bonds as compared to the parent molecule. This shows that the substitution increases the strength of the N−N bonds of 1,2,4,5-tetrazine. Among the 1,2,4,5-tetrazine derivatives with double substituents, the bond orders of B5, B7, and B10 are relatively small and are 0.1137, 0.1471, and 0.1076, respectively. According to the principle of the smallest bond order (PSBO),[29] it may be inferred

TABLE 11: Calculated Bond Dissociation Energies (BDE, kJ/mol) for $A-B(g) \rightarrow A\cdot(g) + B\cdot(g)$ and Bond Overlap Populations of the Weakest Bonds for the 1,2,4,5-Tetrazine Derivatives Together with RDX and HMX at the B3LYP/6-311G Level**[a]

compd	P_{N-N}	P_{C-R}	$P_{N-R'}$	BDE^0	BDE_{ZPE}
B1			0.2161	332.21 (728.44)[b]	316.59 (705.33)
B2	0.3322			328.94	313.88
B3			0.2712	259.36	227.80
B4			0.1699	142.49	122.38
B5		0.1137		308.52 (527.74)	293.08 (510.23)
B6		0.2191		267.10	250.53
B7		0.1471		235.42	218.29
B8	0.2861			338.10	321.73
B9		0.2611		366.54	356.90
B10		0.1076		288.81 (404.35)	273.13 (385.06)
B11			0.1779	135.33	116.40
B12			0.2365	274.89	264.32
A1			0.2094	314.69 (741.95)	296.30 (717.80)
A2	0.3194			319.67	302.76
A3			0.2603	276.25	243.89
A4			0.1656	127.48	107.93
A5		0.1107		306.67 (528.33)	290.42 (510.31)
A6		0.2149		264.72	247.68
A7		0.1471		239.95	222.11
A8	0.2834			322.10	303.04
A9		0.2574		364.36	354.36
A10		0.1314		286.37 (401.21)	268.50 (381.48)
S[c]	0.2835			297.76	276.53
RDX		0.1376		166.19	145.62
HMX		0.1382		178.77	160.41

[a] BDE^0 denotes the bond dissociation energies without zero-point energy corrections, while BDE_{ZPE} denotes the bond dissociation energies including zero-point energy corrections. [b] The values in parentheses are the bond dissociation energies of the bonds with the smallest bond overlap populations. [c] S stands for 1,2,4,5-tetrazine.

that the thermal stability of B5, B7, and B10 is relatively bad. Similar conclusions are also drawn from the bond orders of the 1,2,4,5-tetrazine derivatives with single substituent (A1−10).

Bond dissociation energy (BDE) provides useful information for understanding the stability of the title compounds. It should be pointed out that we select the weakest C−R bond or N−R′ as the breaking bond based on the bond overlap populations at the B3LYP/6-311G** level. The bond overlap populations and bond dissociation energies (BDE) of the weakest bonds for the 1,2,4,5-tetrazine derivatives are listed in Table 11. From the BDE^0 and BDE_{ZPE} values, it is found that the BDE values without zero-point energy correction are larger than those including zero-point energy corrections. However, the order of the dissociation energies is not affected by the zero-point energies. When the $-N_3$, $-NH_2$, −CN, −OH, or −Cl group is attached to the ring, the BDE_{ZPE} value increases, while attachment of another group such as $-NHNH_2$, $-NHNO_2$, $-NO_2$, $-NF_2$, or −COOH will make the BDE_{ZPE} decrease. The calculated BDE can be used to measure the relative order of thermal stability for energetic materials.[50,51] Therefore, it can be deduced that substitutions of the $-N_3$, $-NH_2$, −CN, −OH, or −Cl group are very useful for increasing the thermal stability of 1,2,4,5-tetrazine. Compared with the commonly used explosives RDX (1,3,5-trinitro-1,3,5-triazinane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) the 1,2,4,5-tetrazine derivatives have higher BDE_{ZPE} values except for B4, B11, and A4. This indicates that most of the substituted 1,2,4,5-tetrazines have high thermal stability, in agreement with previous experimental reports.[12,13]

It is interesting to note that the $N-N_2$ bond of B1 has a relatively low bond order of 0.2161 but the highest BDE_{ZPE} value of 705.33 kJ/mol among the weakest bond of the substituted 1,2,4,5-tetrazines. However, the N−N bond in the ring for B1 has higher bond order (0.2919) but lower BDE_{ZPE} (316.59 kJ/mol) compared to the $N-N_2$ bond of B1. A similar situation is also found in B5 and B10. The initial step should be via ring cleavage in thermal decompositions. Therefore, to judge the thermal stability of the 1,2,4,5-tetrazine derivatives is not by the bond order simply, but it is necessary to depend on the BDE_{ZPE}. As is evident in Table 11, the B derivatives basically have higher BDE than A. This indicates that the increasing substituent could strengthen the thermal stability. By analyzing the structure of the compounds, it is easy to find that the 1,2,4,5-tetrazine derivatives with double substituents have symmetric structures. This symmetry can delocalize the π electron cloud density of the ring and so make the stability of the compound increase.

3.3. Predicted Detonation Properties. Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 12 presents calculated detonation velocities (D) and pressures (P) of the 1,2,4,5-tetrazine derivatives together with available experimental data.[18,19,48,52] For a comparison, the experimental detonation performances of two known explosives RDX and HMX are also listed in this table.[53] To validate the reliability of the empirical Kamlet−Jacobs formula, the detonation velocity was also calculated using the Stine method[54]

$$D = 3.69 + \rho_0[13.85n_C + 37.74n_N + 68.11n_O + 3.95n_H + 0.1653\Delta H_f^0(s)]/M \quad (13)$$

where D is the detonation velocity in km/s, ρ is the density of a compound in g/cm^3, $\Delta H_f^0(s)$ is the solid-phase enthalpy of formation in kJ/mol, n_C, n_N, n_O, and n_H are the numbers of atoms C, N, O, and H, respectively, and M is the molecular mass of the compound. Figure 2 presents a comparison of the detonation velocities of the substituted 1,2,4,5-tetrazine obtained from the Kamlet−Jacobs formula with those from the Stine method. Qualitatively, the calculated results by the Kamlet−Jacobs formula reproduce the variation trend of the detonation velocity by the Stine method. It is seen from Table 12 that the detonation velocities with the Kamlet−Jacobs formula are closer to available experimental data than those with the Stine method. Shreeve et al.[55] also used the Kamlet−Jacobs formula to calculate the detonation properties of the energetic nitrogen-rich salts. These suggestions show that Kamlet−Jacobs formula is proper to predict the detonation properties of the 1,2,4,5-tetrazine derivatives.

As is evident in Table 12, the calculated detonation properties of the 1,2,4,5-tetrazine derivatives agree well with available experimental values. Although the error or limitation of the calculation method leads to the predicted D and P somewhat deviating from those from experiment, these results are still reliable and meaningful. The 1,2,4,5-tetrazine derivatives with different substituent groups have different ρ values, for example, the largest value and the smallest one is 2.10 and 1.49 g·cm^{-3}, respectively. This makes the derivatives have different D and P values. Most of the derivatives increase the D and P values as compared to the parent 1,2,4,5-tetrazine except for the −CN, $-NH_2$, and −OH substituents. As the number of subtituent increases, the ρ, D, and P values of the substituted 1,2,4,5-tetrazines enhance except for the $-NHNH_2$ and −CN substituents. It is observed from Table 12 that the ρ values of B6, B7, and A6 are very high and close to 1.9 g·cm^{-3}. Moreover, their

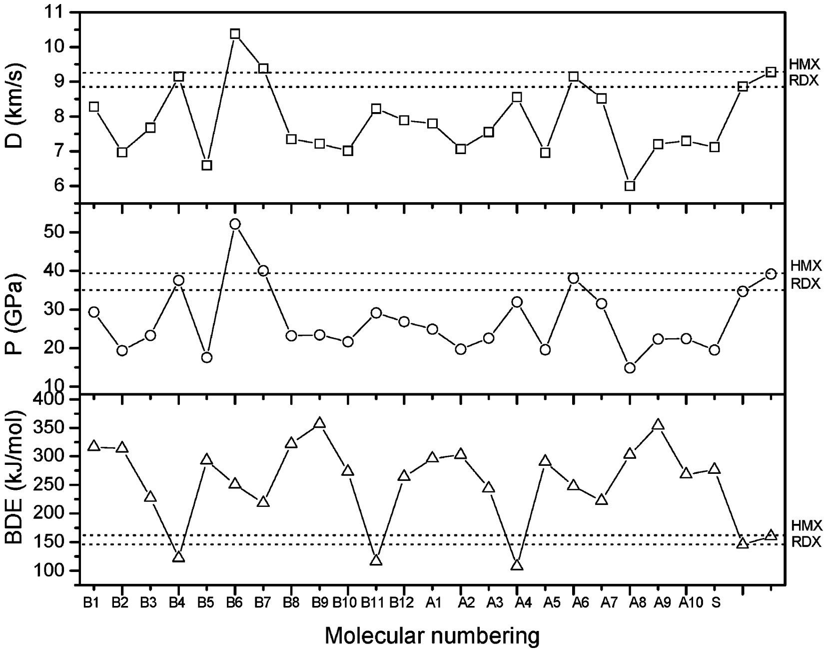

Figure 3. Detonation properties and dissociation energies of the weakest bonds for the substituted 1,2,4,5-tetrazines.

TABLE 12: Predicted Detonation Properties of the 1,2,4,5-Tetrazine Derivatives Together with RDX and HMX[a]

compd	V (cm^3/mol)[b]	φ[c]	ρ (g/cm^3)	D (km/s)	P (GPa)
B1	97.17	6.201	1.70	8.28	29.35
B2	73.78	5.080	1.52	6.97	19.32
B3	94.70	6.251	1.50 (1.56)[18]	7.68 (7.54)[18]	23.26
B4	110.38	7.017	1.83	9.15	37.50
B5	85.35	4.392	1.55	6.59	17.53
B6	87.48	7.412	2.10	10.38	52.16
B7	91.73	6.883	1.88	9.38	40.01
B8	66.90	5.125	1.70	7.35	23.19
B9	81.45	4.434	1.84	7.22	23.41
B10	95.59	4.391	1.78	7.01	21.64
B11	92.14	6.214	1.71 (1.82)[48]	8.23	29.10
B12	84.50	6.472	1.72 (1.83)[19]	7.89 (8.26)[52]	26.86 (24.2)[52]
A1	77.61	5.974	1.59	7.80	24.93
A2	65.06	5.274	1.49	7.07	19.68
A3	74.50	5.973	1.50	7.55	22.56
A4	81.11	6.422	1.75	8.56	31.95
A5	69.18	4.841	1.55	6.96	19.52
A6	70.6	6.641	1.88	9.15	38.13
A7	73.11	6.261	1.74	8.52	31.52
A8	60.93	3.691	1.61	6.00	14.88
A9	67.60	4.874	1.72	7.20	22.35
A10	76.44	5.285	1.65	7.30	22.38
S[d]	56.94	6.024	1.44	7.12	19.47
RDX	124.91	7.038	1.78(1.82)[53]	8.87(8.75)[53]	34.67(34.00)[53]
HMX	157.50	7.123	1.88(1.91)[53]	9.28(9.10)[53]	39.19(39.00)[53]

[a] The values in parentheses are the experimental values from refs 18, 19, 48, 52, and 53. [b] The average volumes are from 100 single-point calculations at the B3LYP/6-31G* level. [c] A characteristic value relates to both the HOF and the molecular stoichiometry of an explosive.[43] [d] S stands for 1,2,4,5-tetrazine.

D and P values are very high and close to 9.0 km·s^{-1} and 40.0 GPa, respectively. It is also found that B6, the derivative with two $-NF_2$ groups, has the largest ρ, D, and P values among these derivatives. This shows that the substitutions of the $-NF_2$ or $-NO_2$ group are useful for increasing the densities and detonation properties of the 1,2,4,5-tetrazine derivatives.

3.4. Potential Candidates for HEDMs. Most of the nitrogen-rich compounds have very high positive heats of formation rather than from oxidation of the carbon backbone, as with traditional energetic materials.[56,57] However, high heats of formation are usually unfavorable for the stability of a compound. Therefore, a good nitrogen-rich HEDM candidate not only has excellent detonation properties but also could exist stably. Figure 3 presents the detonation properties and dissociation energies of the weakest bonds for the substituted 1,2,4,5-tetrazines together with commonly used explosives RDX and HMX.

It is seen that the derivatives B6, B7, and A6 have higher *D* and *P* than RDX. However, only B6 have good detonation performance (*D* and *P*) over HMX. Most of the substituted 1,2,4,5-tetrazines have higher BDE for the weakest bonds as compared to RDX and HMX. On the basis of the BDE for the initial steps in the thermal decompositions, it may be inferred that most 1,2,4,5-tetrazines derivatives are more insensitive to thermal and impact. On the basis of the above suggestions, it may be concluded that only B6, B7, and A6 have good detonation performance (*D* and *P*) and thermal stability (BDE) close to RDX and HMX. Therefore, B6, B7, and A6 may be considered potential candidates of HEDMs with less sensitivity and higher performance.

Although B1−3 and B11−12 have been successfully synthesized, some detonation properties are still lacking. In addition, the syntheses of other energetic compounds have not been reported yet. Thus, further investigations are still needed.

4. Conclusions

In this work, we calculated the heats of formation (HOFs) for a series of 1,2,4,5-tetrazines derivatives using HF, MP2, and DFT as well as semiempirical methods. The results show that the HOFs by DFT and MP2 methods are in agreement with available experimental results. Basis sets slightly affect HOFs and larger basis sets tend to produce slightly higher HOFs. It is found that the $-CN$ or $-N_3$ group plays a very important role in increasing the HOF values of the 1,2,4,5-tetrazine derivatives.

An analysis of the bond dissociation energies for the weakest bonds indicates that substitutions of the $-N_3$, $-NH_2$, $-CN$, $-OH$, or $-Cl$ group are favorable for enhancing the thermal stability of 1,2,4,5-tetrazine, but the $-NHNH_2$, $-NHNO_2$, $-NO_2$, $-NF_2$, or $-COOH$ group produces opposite effects. The calculated detonation velocities and detonation pressures indicate that the $-NF_2$ or $-NO_2$ group is very helpful for enhancing the detonation performance for the derivatives, but the case is quite the contrary for the $-CN$, $-NH_2$, or $-OH$ group. Considering the detonation performance and thermal stability, B6, B7, and A6 may be regarded as potential candidates of HEDMs. These results provide basic information for the molecular design of novel HEDMs.

Acknowledgment. This work was supported by the NSAF Foundation of National Natural Science Foundation of China and China Academy of Engineering Physics (grant no. 10876013), the Research Fund for the Doctoral Program of Higher Education, and the Project-sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References and Notes

(1) Fried, L. E.; Manaa, M. R.; Pagoria, P. F.; Simpson, R. L. *Annu. Rev. Mater. Res.* **2001**, *31*, 291.

(2) Strout, D. L. *J. Phys. Chem. A* **2004**, *108*, 10911.

(3) Nguyen, M. T. *Coord. Chem. Rev.* **2003**, *244*, 93.

(4) Xu, X. J.; Xiao, H. M.; Ju, X. H.; Gong, X. D.; Zhu, W. H. *J. Phys. Chem. A* **2006**, *110*, 5929.

(5) Rice, B. M.; Byrd, E. F. C.; Mattson, W. D. *Struct. Bonding (Berlin)* **2007**, *125*, 85.

(6) Klapötke, T. M. *Struct. Bonding (Berlin)* **2007**, *125*, 153.

(7) Benson, F. R. *The High Nitrogen Compounds*; Wiley-Interscience: New York, 1984.

(8) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1791.

(9) Kerth, J.; Lobbecke, S. *Propellants, Explos., Pyrotech.* **2002**, *27*, 111.

(10) Neutz, J.; Grosshardt, O.; Schaufele, S.; Schuppler, H.; Schweikert, W. *Propellants, Explos., Pyrotech.* **2003**, *28*, 181.

(11) Huynh, M. H. V.; Hiskey, M. A.; Hartline, E. L.; Montoya, D. P.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4924.

(12) Churakov, A. M.; Smirnov, O. Y.; Ioffe, S. L.; Strelenko, Y. A.; Tartakovsky, V. A. *Eur. J. Org. Chem.* **2002**, *14*, 2342.

(13) Huynh, M. H. V.; Hiskey, M. A.; Pollard, C. J.; Montoya, D. P.; Hartline, E. L.; Gilardi, R. D. *J. Energy Mater.* **2004**, *22*, 217.

(14) Saracoglu, N. *Tetrahedron* **2007**, *63*, 4199.

(15) Huynh, M. H. V.; Hiskey, M. A.; Chavez, D. E.; Naud, D. L.; Gilardi, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 12537.

(16) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Org. Lett.* **2004**, *6*, 2889.

(17) Huynh, M. H. V.; Hiskey, M. A.; Archuleta, J. G.; Romemer, E. L.; Gilardi, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5658.

(18) Hiskey, M. A.; Chavez, D. E.; Naud, D. L. In Sensitive High Nitrogen Compounds. NTIS No: DE-2001-776133, 2001.

(19) Chavez, D. E.; Hiskey, M. A. *J. Energy Mater.* **1999**, *17*, 357.

(20) Talawar, M. B.; Sivabalan, R.; Senthilkumar, N.; Prabhu, G.; Asthana, S. N. *J. Hazard. Mater. A* **2004**, *113*, 11.

(21) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(22) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(23) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(24) Stewart, J. J. P. *J. Mol. Model.* **2004**, *10*, 155.

(25) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. Hehre, W. J. *Critical Assessment of Molecular Electronic Structure Methods; Wavefunction*; Irvine, CA, 1955.

(26) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(27) Seminario, J. M.; Politzer, P. *Modern Density Functional Theory: A Tool for Chemistry*; Elsevier: Amsterdam, 1995.

(28) Chen, Z. X.; Xiao, J. M.; Xiao, H. M.; Chiu, Y. N. *J. Phys. Chem. A* **1999**, *103*, 8062.

(29) Xiao, H. M.; Chen, Z. X. *The Modern Theory for Tetrazole Chemistry, 1st ed.*; Science Press: Beijing, 2000.

(30) Chen, P. C.; Chieh, Y. C.; Tzeng, S. C. *J. Mol. Struct. (THEOCHEM)* **2003**, *634*, 215.

(31) Ju, X. H.; Li, Y. M.; Xiao, H. M. *J. Phys. Chem. A* **2005**, *109*, 934.

(32) Hahre, W. J.; Radom, L.; Schleyer, P. V. R.; Pole, J. A. *Ab Initio Molecular Orbital Theory*, 1st ed.; Wiley-Interscience: New York, 1986; p *386*.

(33) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **2000**, *499*, 137.

(34) Wang, F.; Xu, X. J.; Xiao, H. M.; Zhang, J. *Acta. Chim. Sin.* **2003**, *61*, 1939.

(35) Ju, X. H.; Wang, X.; Bei, F. L. *J. Comput. Chem.* **2005**, *26*, 1263.

(36) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(37) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(38) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(39) Mills, I.; Cvitas, T.; Homann, K.; Kallay, N.; Kuchitsu, K.; *Quantities, Units, and Symbols in Physical Chemistry*; Blackwell Scientific Publications: Oxford, 1988.

(40) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople J. A. *Gaussian 98*, Revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.

(42) Kamlet, M. J.; Jacobs, S. J. *J. Chem. Phys.* **1968**, *48*, 23.

(43) Qiu, L.; Xiao, H. M.; Gong, X. D.; Ju, X. H.; Zhu, W. H. *J. Hazard. Mater.* **2007**, *141*, 280.

(44) David, R. L. *Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, 2003−2004, Sect 5.

(45) Dean, J. A. *LANGE'S Handbook of Chemistry*, 15th ed.; McGraw-Hill Book Co.: New York, 1999; Chapter 6.

(46) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Chemistry Web Book. U.S. Secretary of Commerce on behalf of the U.S.A.; All rights reserved: National Institute of Standards and Technology, 1998.

(47) Chen, Z. X.; Xiao, H. M.; Song, W. Y. *J. Mol. Struct (THEOCHEM)* **1999**, *460*, 167.

(48) Singh, R. P.; Gao, H. X.; Meshri, D. T.; Shreeve, J. M. *Struct. Bonding (Berlin)* **2007**, *125*, 35.

(49) Scott, A. P.; Radom, L. J. *J. Phys. Chem.* **1996**, *100*, 16502.

(50) Owens, F. J. *J. Mol. Struct. (THEOCHEM)* **1996**, *370*, 11.

(51) Rice, B. M.; Sahu, S.; Owens, F. J. *J. Mol. Struct. (THEOCHEM)* **1996**, *583*, 69.

(52) Licht, H. H.; Ritter, H. *J. Energy Mater.* **1994**, *12*, 223.

(53) Talawar, M. B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A. K.; Gandhe, B. R.; Subhananda Rao, A. *J. Hazard. Mater.* **2009**, *161*, 589.

(54) Stine, J. R. *J. Energy Mater.* **1990**, *8*, 41.

(55) Sing, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584.

(56) Zhang, M. X.; Eaton, P. E.; Gilardi, R. D. *Angew. Chem.* **2000**, *112*, 422.

(57) Zhang, M. X.; Eaton, P. E.; Gilardi, R. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 401.

JP902295V