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Design and selection of nitrogen-rich bridged di-1,3,5-triazine derivatives with high energy and reduced sensitivity

Yong Pan · Weihua Zhu · Heming Xiao

Abstract The heats of formation (HOFs), electronic structures, energetic properties, and thermal stabilities of a series of energetic bridged di-1,3,5-triazine derivatives with different substituents and linkages were studied using density functional theory. It was found that the groups $-N_3$ and $-N=N-$ are effective structural units for improving the HOF values of the di-1,3,5-triazine derivatives. The effects of the substituents on the HOMO–LUMO gap combine with those of the bridge groups. The calculated detonation velocities and detonation pressures indicate that substituting the $-ONO_2$, $-NF_2$, or $-N=N-$ group is very useful for enhancing the detonation performance of these derivatives. Analysis of the bond dissociation energies for several relatively weak bonds suggests that most of the derivatives have good thermal stability. On the whole, the $-NH_2$, $-N_3$, $-NH-$, and $-CH=CH-$ groups are effective structural units for increasing the thermal stabilities of the derivatives. Based on detonation performance and thermal stability, nine of the compounds can be considered potential candidates for high energy density materials with reduced sensitivity.

Keywords Density functional theory · Di-1,3,5-triazine derivatives · Heat of formation · Detonation performance · Thermal stability

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Introduction

Five- or six-membered nitrogen-rich heterocyclic compounds have been investigated extensively to screen for promising candidates for high-energy density materials (HEDMs) [1–18], as these compounds are very dense, have highly positive heats of formation (HOFs), good detonation properties, and high thermal stabilities. Among them, the heterocycle 1,3,5-triazine (or s-triazine) is an effective structural unit for synthesizing highly energetic materials due to its high nitrogen content (53.8%). Many studies [19–31] have focused on the synthesis and properties of energetic 1,3,5-triazine derivatives. Some of them have shown great potential as energetic additives for high explosive/rocket propellant formulations and pyrotechnic ingredients. For example, 2,4,6-trinitro-1,3,5-triazine (TNTA) could be a new, powerful HEDM [23]. 4,6-Dinitroamino-1,3,5-triazine-2(1H)-one (DNAM) was evaluated as a potential component of composite propellant formulations [24–26]. Hexahydro-1,3,5-trinitro-s-triazine (RDX) has been used as an energetic additive in high explosive propellant formulations and pyrotechnic ingredients since it was first synthesized [29, 30]. Remarkably, the experimentally measured HOF for 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine is the highest reported for any energetic material [31]. However, there is still lacking systematic and comprehensive molecular design for di-1,3,5-triazine-based HEDMs.

Over the past several decades, due to the development of computers and computational chemistry, theoretical studies have gained acceptance as a useful research tool for investigating the structures and properties of energetic compounds [2–4]. Properties are often manipulated by making structural modifications. Therefore, the selection of di-1,3,5-triazine-based molecules with high energies and low sensitivities is the primary step in the design and synthesis of new HEDMs.

The formation of molecular complexes (e.g., di-, tri-, oligo-, and polymers) is a conceivable way to increase density and stability and to improve the material properties of propellants and explosives [23]. Some researchers have paid much attention to the effects of bridge groups on the HOFs, thermal stabilities, and detonation properties of energetic heterocyclic compounds. Previous studies [31] on the synthesis and properties of novel hydrazo- and azo-bridged 1,3,5-triazines indicated that the hydrazo (–NH–NH–) and azo (–N=N–) linkages not only desensitize but also dramatically increase the melting point of the 1,3,5-triazine derivatives. Joo and Shreeve [32] reported that nitroiminotetrazoles linked by –CH2–CH2– have highly positive HOFs and good detonation properties. Another report [33] noted that the azo bridge (–N=N–) played a very important role in increasing the HOF values of difurazan derivatives, and that the –NH–NH–, –N=N–, and –N(O)=N– groups were effective bridges for enhancing thermal stability. These suggestions show that combining high-nitrogen heterocycles with different bridges can improve the performance of energetic materials.

In this paper, we report a systematic study of the HOFs, electronic structures, energetic properties, and thermal stabilities of a series of bridged di-1,3,5-triazine derivatives with various substituents (–NH2, –NO2, –ONO2, –NF2, –N3) and different linkages (–CH2–, –NH–, –CH2–CH2–, –NH–NH–, –CH=CH–, –N=N–) based on the use of density functional theory (DFT). The main purpose of this study was to investigate the roles of different substituents and linkages in the design of efficient high energy density compounds.

The remainder of this paper is organized as follows. A brief description of the computational method we employed in this study is given in the following section. The results of the study and a discussion of them are presented in the section after that, and a summary of our conclusions is provided in the final section.

Computational methods

Figure 1 presents the molecular frameworks of the series of bridged di-1,3,5-triazines (labeled A1–A6, B1–B6, C1–C6, D1–D6, E1–E6, F1–F6, and G1–G6) studied in this work. The isodesmic reaction method was employed to calculate their HOFs, using the total energies obtained from DFT-B3LYP/6-31G(d,p) calculations. This approach has been demonstrated to reliably predict the HOFs of many organic systems via isodesmic reactions [3, 4, 34–39]. We designed isodesmic reactions in which the numbers of all kinds of bonds were kept constant, in order to decrease the HOF calculation
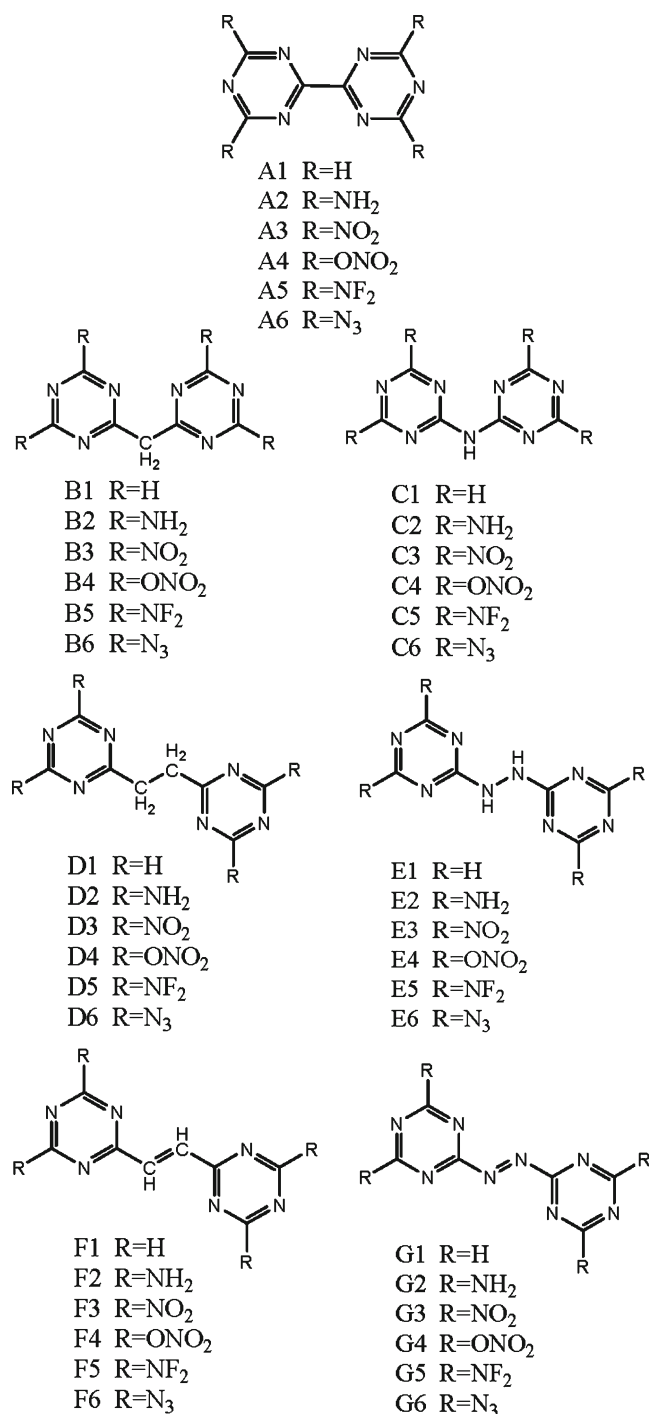
Fig. 1 Molecular frameworks of the bridged di-1,3,5-triazines (labeled A1–A6, B1–B6, C1–C6, D1–D6, E1–E6, F1–F6, and G1–G6)

errors. Because the reactants and products are very similar from an electronic perspective in isodesmic reactions, the errors in the electronic energies can be counteracted, so the errors in the calculated HOF can be greatly reduced. In these designed reactions, the basic structural unit of the 1,3,5-triazine skeleton remains the same, but big molecules are changed into

small ones. This method has been shown to be reliable [3, 33, 38–43].

$$\text{(1)}$$
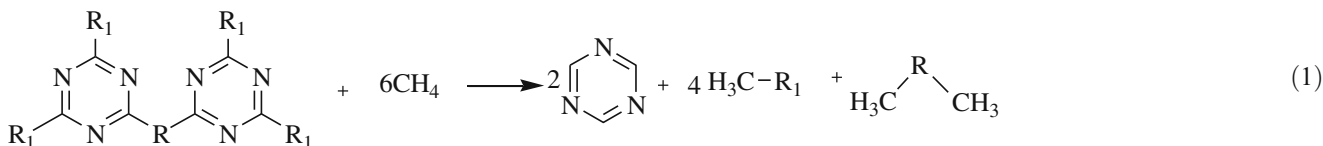
where $R_1 = $ –H, –NH$_2$, –NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$. R $=$ –, –CH$_2$–, –NH–, –CH$_2$CH$_2$–, –NH–NH–, –CH$_2$=CH$_2$–, –NH=NH–.

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

$$\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R}, \tag{2}$$

where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of the reactants and products at 298 K, respectively. As the experimental HOFs of CH$_3$NF$_2$, CH$_3$N$_3$, and CH$_3$N=NCH$_3$ are unavailable, additional calculations were carried out. The HOF of CH$_3$NF$_2$ was calculated by the replacement reaction CH$_3$NH$_2$ + F$_2$ → CH$_3$NF$_2$ + H$_2$ using the G2 theory [42, 43]. The HOF values of CH$_3$N$_3$ and CH$_3$N=NCH$_3$ were obtained at the G2 level from the atomization reaction C$_a$H$_b$N$_c$ → aC$_{(g)}$ + bH$_{(g)}$ + cN$_{(g)}$. The experimental HOFs for the reference compounds 1,3,5-triazine, CH$_4$, CH$_3$NH$_2$, CH$_3$NO$_2$, CH$_3$ONO$_2$, CH$_3$NHCH$_3$, CH$_3$CH$_3$, CH$_3$CH$_2$CH$_3$, CH$_3$CH$_2$CH$_2$CH$_3$, CH$_3$NHNHCH$_2$, and CH$_3$CH=CHCH$_3$ are available. The most important task then is to compute ΔH_{298K}. ΔH_{298K} can be calculated using the following expression:

$$\begin{aligned} \Delta H_{298K} &= \Delta E_{298K} + \Delta(PV) \\ &= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT, \end{aligned} \tag{3}$$

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 (ZPE) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. $\Delta(PV)$ in Eq. 3 is the PV work term, which equals ΔnRT for ideal gas reactions. For the isodesmic reactions considered here, $\Delta n = 0$, so $\Delta(PV) = 0$.

Since the condensed phases of most energetic compounds are solid, calculating detonation properties requires knowledge of the solid-phase heat of formation ($\Delta H_{f,solid}$). According to Hess's law of constant heat summation [44], the gas-phase heat of formation ($\Delta H_{f,gas}$) and heat of sublimation (ΔH_{sub}) can be used to evaluate the solid-phase heats of formation:

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub}. \tag{4}$$

The isodesmic reactions used to obtain the HOFs of the di-1,3,5-triazine derivatives at 298 K are as follows:

Politzer et al. [45–47] found that the heat of sublimation correlates well with the molecular surface area and the electrostatic interaction index $\nu\sigma_{tot}^2$ for energetic compounds. The empirical expression for this approach is as follows:

$$\Delta H_{sub} = aA^2 + b\left(\nu\sigma_{tot}^2\right)^{0.5} + c, \tag{5}$$

where A is the surface area of the 0.001 electrons/bohr^3 isosurface of the electronic density of the molecule, ν describes the degree of balance between positive potential and negative potential on the isosurface, and σ_{tot}^2 is a measure of the variability of the electrostatic potential on the molecular surface. The coefficients a, b, and c were determined by Rice et al.: $a = 2.670 \times 10^{-4}$ kcal mol^{-1} A^{-4}, $b = 1.650$ kcal mol^{-1}, and $c = 2.966$ kcal mol^{-1} [48]. The descriptors A, ν, and σ_{tot}^2 were calculated using the computational procedures described by Felipe et al. [49]. This approach has been demonstrated to reliably predict the heats of sublimation of many energetic compounds [48, 50].

The detonation velocity and pressure were estimated by the Kamlet–Jacobs equations [51] as

$$D = 1.01\left(N\overline{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho) \tag{6}$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2}, \tag{7}$$

where each term in Eqs. 6 and 7 is defined as follows: D, the detonation velocity (km/s); P, the detonation pressure (GPa); N, the moles of detonation gases per gram of explosive; $\overline{M}$, the average molecular weight of these gases; Q, the heat of detonation (J/g); and ρ, the loaded density of explosives (g/cm^3). For known explosives, Q and ρ can be measured experimentally; thus, D and P can be calculated according to Eqs. 6 and 7. However, for some compounds, Q and ρ cannot be evaluated from experimental measurements. Therefore, to estimate their D and P, we first need to calculate Q and ρ.

For each di-1,3,5-triazine derivative, the theoretical density was obtained from the molecular weight divided by the average molecular volume. The volume was defined as that inside the density contour of 0.001 electrons/bohr^3, which was evaluated using a Monte Carlo integration. We

performed 100 single-point calculations for each optimized structure to get the average volume at the B3LYP/6-31G(d,p) level [52]. The crystal density can be improved by introducing the interaction index $\nu\sigma_{tot}^2$ [53]:

$$\rho = \beta_1 \left(\frac{M}{V}\right) + \beta_2 \left(\nu\sigma_{tot}^2\right) + \beta_3, \tag{8}$$

in which M is the molecular mass (g/molecule) and V is the volume of the isolated gas molecule (cm^3/molecule). The coefficients β_1, β_2, and β_3 are 0.9183, 0.0028, and 0.0443, respectively [53].

The heat of detonation Q was evaluated by the HOF difference between the products and explosives according to the principle of exothermic reactions, i.e., all the N atoms combine into N_2, F atoms form HF with H atoms or combine into F_2 without H atoms, and oxygen atoms form H_2O before CO_2. If the content of O is not sufficient to satisfy full oxidation of the H and C atoms, the remaining H atoms will convert into H_2, and C atoms will exist as solid-state C. In the Kamlet–Jacobs equations, the detonation products are assumed to be CO_2 (or C), H_2O (or H_2 or HF or F_2), and N_2, so the energy released in the decomposition reaction is maximized. Using the values of ρ and Q, the corresponding D and P values can be evaluated. The theoretical molecular density used in this work was slightly greater than the practical loaded density. Therefore, according to the Kamlet–Jacobs equations, the values of D and P can be regarded as their upper limits.

The strength of bonding, which can be evaluated via the bond dissociation energy, is fundamental to understanding chemical processes [54]. The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of the reaction $A–B_{(g)} \rightarrow A\cdot_{(g)} + B\cdot_{(g)}$, which is the bond dissociation enthalpy of molecule A–B by definition [55]. For many organic molecules, the terms "bond dissociation energy" (BDE) and "bond dissociation enthalpy" often appear interchangeably in the literature [56]. Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms o

$$BDE_0(A - B) \rightarrow E_0(A\cdot) + E_0(B\cdot) - E_0(A - B). \tag{9}$$

The bond dissociation energy corrected for the zero-point energy (ZPE) can be calculated by

$$BDE(A - B)_{ZPE} = BDE_0(A - B) + \Delta E_{ZPE}, \tag{10}$$

where ΔE_{ZPE} is the difference between the ZPEs of the products and the reactants.

The calculations were performed with the Gaussian 03 package. The optimizations were performed without any symmetry restrictions, using the default convergence criteria in the software. All of the optimized structures were found to be true local energy minima on the potential energy surfaces, without imaginary frequencies.

Results and discussion

Gas-phase heats of formation

Here we investigate the effects of different substituents and linkages on the gas-phase heats of formation ($\Delta H_{f,gas}$) of the bridged di-1,3,5-triazine derivatives. Table 1 lists the total energies, ZPEs, and thermal corrections for 14 reference compounds in the isodesmic reactions. The experimental HOFs of CH_4, CH_3NH_2, CH_3NO_2, CH_3ONO_2, CH_3NHCH_3, $CH_3CH_2CH_3$, $CH_3CH_2=CH_2CH_3$, $CH_3NH=NHCH_3$, and 1,3,5-triazine were taken from [57–59], respectively. The HOF values of CH_3N_3 and $CH_3N=NCH_3$ were calculated at the G2 level from the atomization reactions. The HOF of CH_3NF_2 was obtained from the replacement reaction: $CH_3NH_2 + F_2 \rightarrow CH_3NF_2 + H_2$, and was close to the values reported in [42, 43]. To validate the reliability of our results, the HOFs of CH_4, CH_3CH_3, $CH_3CH_2CH_3$, $CH_3CH_2CH_2CH_3$, CH_3NH_2, CH_3NHCH_3, and 1,3,5-triazine were also calculated at the G2 level from the atomization reaction. The results show that these HOF values are very close to their corresponding experimental values [50–52], with relative errors of only 3.83%, 1.80%, 1.62%, 0.36%, 0.94%, 3.01%, and 0.51%, respectively. Therefore, the HOF values from the G2 calculations are expected to be reliable in this work.

Table 2 presents the total energies, ZPEs, thermal corrections, and $\Delta H_{f,gas}$ values for the bridged di-1,3,5-triazine derivatives. A comparison of our calculated results with available experimental values indicated that our results are credible. For the A series, when the substituent is $–N_3$, the $\Delta H_{f,gas}$ value of its substituted di-1,3,5-triazine (A6) increases compared with the unsubstituted case (A1), whereas the opposite is true for the substituents $–NH_2$, $–NO_2$, $–ONO_2$, and $–NF_2$. This also holds for the E series. However, for the B, C, D, F, and G series, the situation is different. The substitution of $–NO_2$ or $–N_3$ increases the $\Delta H_{f,gas}$ values of the parent bridged di-1,3,5-triazines (B1, C1, D1, F1, or G1), while the substitution of $–NH_2$, $–ONO_2$, or $–NF_2$ has the opposite effect. When the H atoms of the di-1,3,5-triazines are replaced with $–N_3$, the resulting $\Delta H_{f,gas}$ value is the largest in the series. In addition, it is worth noting that substitution of the group $–ONO_2$ greatly decreases the $\Delta H_{f,gas}$ values compared with those of the parent di-1,3,5-triazines (A1). The same is true of the carbon-bridged di-1,3,5-triazines (B, D, and F) and the nitrogen-bridged di-1,3,5-triazines (C, E, and G). These observations show that the $–N_3$ group plays a very important role in increasing the $\Delta H_{f,gas}$ values of the bridged di-1,3,5-triazines, while substituting $–ONO_2$ greatly reduces $\Delta H_{f,gas}$.

Table 1 Calculated total energies (E_0), zero-point energies (ZPE, kJ mol^{-1}), thermal corrections (H_T, kJ mol^{-1}), and heats of formation (HOFs, kJ mol^{-1}) for the reference compounds [a]

Compound	E_0	ZPE	H_T	HOF [c]	HOF [b]	HOF
CH_4	−40.5240	0.0441	10.03	−77.46	−74.60	
CH_3CH_3	−79.8387	0.0734	11.75	−85.51	−84.00	
$CH_3CH_2CH_3$	−119.1553	0.1016	14.64	−105.48	−103.80	
$CH_3CH_2CH_2CH_3$	−158.4719	0.1296	18.04	−126.06	−125.60	
CH_3NH_2	−95.8637	0.0629	11.51	−22.71	−22.50	
CH_3NHCH_3	−135.1740	0.0908	14.22	−19.06	−18.50	
1,3,5-Triazine	−280.3687	0.0654	13.57	227.01	225.85	
$CH_3NHNHCH_3$	−190.4899	0.1076	17.43		92.20	
$CH_3CH=CHCH_3$	−157.2386	0.1060	17.18		−11.40	
CH_3NO_2	−245.0134	0.0490	14.07		−80.80	
CH_3ONO_2	−320.1935	0.0534	15.77		−124.40	
$CH_3N=NCH_3$	−189.2833	0.0828	16.26	152.54		151.80 [d]
CH_3NF_2	−294.2099	0.0462	13.84	−114.78		−115.23 [d]
CH_3N_3	−204.0972	0.0494	14.43	296.50		296.50 [d]

[a] E_0 and ZPE are in a.u.; H_T and HOF are in kJ mol^{-1}. The scaling factor is 0.98 for the ZPE and 0.96 for H_T [60]

[b] The experimental HOFs were taken from [57–59], respectively

[c] The values are calculated at the G2 level from the atomization reaction or the replacement reaction

[d] The theoretical HOFs were taken from [33, 42, 43], respectively

Solid-phase heats of formation

The solid-phase heat of formation, $\Delta H_{f,solid}$, is an important property for predicting the detonation properties of the energetic materials. The calculated ΔH_{sub} and $\Delta H_{f,solid}$ values of the bridged di-1,3,5-triazines are summarized in Table 2. It was found that, qualitatively, the calculated solid-phase HOFs show the same trend as the gas-phase HOFs. This shows that the trend in the HOFs of the bridged di-1,3,5-triazines observed when the linkages and substituents are varied is similar for the compounds in the gas phase and for those in the solid phase.

Figure 2 displays a comparison of the $\Delta H_{f,solid}$ values for different bridged di-1,3,5-triazine derivatives. The $\Delta H_{f,solid}$ values of the N=N-bridged di-1,3,5-triazines (G series) are higher than those of the directly linked di-1,3,5-triazines (A series) with the same substituents, while for the bridging groups –CH$_2$–, –NH–, and –CH$_2$–CH$_2$–, the opposite is true. However, when the bridge is –NH–NH– or –CH=CH–, the situation is different. Some of the bridged di-1,3,5-triazines have smaller $\Delta H_{f,solid}$ values than the directly linked di-1,3,5-triazines (A series) with the same substituents (E1–5 vs. A1–5; F1–3 vs. A1–3), while others show the opposite behavior (E6 vs. A6; F4–6 vs. A4–6). This shows that the effects of the –NH–NH– and –CH=CH– groups on the $\Delta H_{f,solid}$ values of the di-1,3,5-triazines are coupled to those of the substituents. Thus, incorporating –N=N– into the directly linked di-1,3,5-triazines increases their $\Delta H_{f,solid}$ values. In addition, the substituted di-1,3,5-triazines with the

conjugated bridge –CH=CH– (–N=N–) have higher $\Delta H_{f,solid}$ values than the corresponding ones with the unconjugated bridge –CH$_2$–CH$_2$– (–NH–NH–). This is because the two di-1,3,5-triazines and the conjugated bridge together comprise a large conjugated system. The substituted di-1,3,5-triazines linked by the azo group (–N=N–) have the highest $\Delta H_{f,solid}$ values among the derivatives with the same substituents. This indicates that the –N=N– group is an effective bridge for increasing the $\Delta H_{f,solid}$ values of the bridged di-1,3,5-triazines.

Electronic structure

Table 3 lists the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and the energy gaps ($\Delta E_{LUMO-HOMO}$) for the bridged di-1,3,5-triazine derivatives. For all of the series, when the –NH$_2$ group is attached to the ring, the HOMO energy level increases, whereas attaching other groups such as –NO$_2$, –ONO$_2$, –NF$_2$, or –N$_3$ will decrease the HOMO energy. All series with the substituents –NO$_2$, –ONO$_2$, –NF$_2$, or –N$_3$ have lower LUMO energies than the corresponding unsubstituted di-1,3,5-triazines, whereas those with the –NH$_2$ group have higher LUMO energies. This indicates that different substituents exert different effects on the HOMO and LUMO energies of the bridged di-1,3,5-triazines. In addition, all of the unsubstituted carbon-bridged di-1,3,5-triazines (B1, D1, and F1) have lower HOMO energies than the unsubstituted but directly

Table 2 Calculated total energies (E_0, a.u.), zero-point energies (ZPE, a.u.), thermal corrections (H_T, kJ mol^{-1}), molecular properties, heats of sublimation (kJ mol^{-1}), and heats of formation (kJ mol^{-1}) for the bridged di-1,3,5-triazines [a]

Compound	E	ZPE	H_T	$\Delta H_{f,gas}$	A	ν	σ^2_{tot}	ΔH_{sub}	$\Delta H_{f,solid}$
A(–)									
A1	−559.5398	0.108	25.16	647.11	178.81	0.16	135.00	80.41	566.69
A2	−781.0675	0.175	41.67	398.58	235.46	0.25	235.04	127.03	271.55
A3	−1377.4605	0.115	54.76	530.87	297.23	0.05	230.68	135.31	395.56
A4	−1678.2546	0.130	66.63	161.15	341.66	0.23	111.34	178.07	−16.92
A5	−1574.2683	0.103	56.88	340.01	281.23	0.15	157.71	134.79	205.23
A6	−1213.9267	0.120	53.59	1702.21	314.90	0.23	99.29	156.52	1545.69
B(–C–)									
B1	−598.8662	0.136	28.82	434.46	200.31	0.17	103.55	86.42	348.04
B2	−820.3926	0.203	45.13	188.90	256.35	0.25	204.87	134.92	53.98
B3	−1416.7931	0.143	58.12	470.56	316.66	0.09	201.76	153.38	317.18
B4	−1717.5840	0.159	69.87	108.48	362.32	0.17	87.96	185.70	−77.22
B5	−1613.5984	0.131	60.42	285.15	301.86	0.11	123.07	139.99	145.17
B6	−1253.2539	0.148	57.02	1655.11	335.98	0.25	89.46	170.88	1484.24
C(–N–)									
C1	−614.9268	0.126	27.82	410.90	193.43	0.22	129.81	90.92	319.98
C2	−836.4516	0.192	44.01	169.39	249.55	0.25	185.99	128.67	40.72
C3	−1432.8529	0.133	57.41	448.08	310.76	0.07	248.97	149.85	298.23
C4	−1733.6442	0.148	69.20	85.73	355.08	0.16	117.54	183.24	−97.52
C5	−1629.6586	0.121	59.78	262.63	295.43	0.13	167.14	142.09	120.54
C6	−1269.3132	0.138	56.37	1634.50	329.05	0.25	115.84	170.34	1464.15
D(–C–C–)									
D1	−638.1862	0.164	32.64	403.98	219.95	0.20	82.04	94.42	309.56
D2	−859.7112	0.231	48.50	162.95	274.64	0.24	206.23	145.27	17.68
D3	−1456.1185	0.171	61.35	424.58	331.83	0.13	184.56	169.75	254.83
D4	−1756.9052	0.187	72.88	75.69	362.64	0.20	78.24	186.48	−110.79
D5	−1652.9206	0.160	63.52	249.11	312.11	0.15	108.17	149.26	99.85
D6	−1292.5733	0.177	60.37	1627.09	354.06	0.24	84.78	183.44	1443.65
E(–N–N–)									
E1	−670.2549	0.142	32.27	487.92	208.86	0.24	117.96	98.12	389.80
E2	−891.7775	0.209	47.52	216.82	264.82	0.22	163.07	132.38	84.44
E3	−1488.1864	0.149	61.25	475.41	325.20	0.09	241.60	163.08	312.32
E4	−1788.9728	0.164	73.68	125.67	370.80	0.10	107.77	188.96	−63.29
E5	−1684.9898	0.137	63.87	295.80	310.76	0.11	162.35	149.62	146.18
E6	−1324.6421	0.153	60.91	1709.61 (1753 [b])	344.53	0.25	92.74	177.93	1531.68
F(–C=C–)									
F1	−636.9616	0.142	30.87	496.97	213.83	0.22	86.89	93.79	403.18
F2	−858.4875	0.208	47.33	252.68	269.84	0.22	169.96	136.34	116.34
F3	−1454.8890	0.149	60.40	530.82	330.92	0.10	165.47	163.00	367.82
F4	−1755.6787	0.164	72.22	172.66	376.12	0.16	66.46	192.77	−20.11
F5	−1651.6938	0.137	62.72	347.88	315.91	0.14	94.31	148.96	198.92
F6	−1291.3485	0.153	59.37	1719.70	349.72	0.25	74.01	178.58	1541.12
G(–N=N–)									
G1	−668.9842	0.117	30.37	716.11	207.49	0.21	114.76	94.64	621.47
G2	−890.5149	0.184	46.93	459.58	263.81	0.25	264.03	146.13	313.45
G3	−1486.9038	0.124	59.82	770.19	325.11	0.07	206.32	156.16	614.03
G4	−1787.6993	0.139	71.79	397.26	370.60	0.20	94.00	195.91	201.36
G5	−1683.7076	0.112	80.55	605.94	310.79	0.11	134.98	147.19	458.75
G6	−1323.3703	0.129	58.83	1940.88 (2170 [b])	343.88	0.24	108.92	179.80	1761.08

[a] E_0 and ZPE are in a.u.; H_T and HOF are in kJ mol^{-1}. The scaling factor is 0.98 for ZPE and 0.96 for H_T [60]

[b] The experimental HOFs were taken from [31]
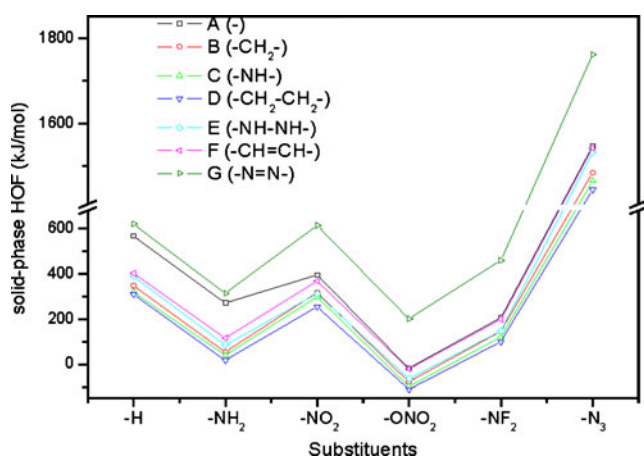
Fig. 2 Comparison of the HOFs of bridged di-1,3,5-triazines with different substituents and linkages

linked di-1,3,5-triazines (A1). However, incorporating the substituent into the ring alters the trend, and furthermore, different substituents have different effects on the HOMO energies of derivatives with different bridges. This shows that the substituents interact predominately with the HOMO orbital for the carbon-bridged di-1,3,5-triazines. For the nitrogen-bridged di-1,3,5-triazines, a similar analysis indicates that the bridge groups also interact mainly with the HOMO orbital. However, the situation is different for their LUMO energies. Incorporating a bridge group of −CH$_2$−, –NH–, –CH$_2$–CH$_2$, or –NH–NH– into an unsubstituted di-1,3,5-triazine increases the LUMO energy compared with the unsubstituted but directly linked di-1,3,5-triazine. Further, introducing the substituent does not affect the sequence of LUMO energies. This indicates that unconjugated bridge groups interact mainly with the LUMO orbital. For the CH=CH- or N=N-bridged di-1,3,5-triazines, a similar analysis indicates that the substituents interact predominately with the LUMO orbital.

Some of the substituted derivatives have larger HOMO–LUMO gaps than the corresponding unsubstituted di-1,3,5-triazines, while others have smaller gaps. For all of the series, when an –NH$_2$ group is attached to the ring, incorporating substituents into the ditriazine increases its HOMO–LUMO gap, whereas attaching –NO$_2$ or –NF$_2$ decreases its HOMO–LUMO gap. A(–NH$_2$, –ONO$_2$, –N$_3$), B–NH$_2$, C–NH$_2$, D–NH$_2$, E–NH$_2$, F(–NH$_2$, –ONO$_2$), and G–NH$_2$ have larger energy gaps than their corresponding unsubstituted molecules, indicating a shift toward higher frequencies in their electronic absorption spectra. However, A(–NO$_2$, –NF$_2$), B(–NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$), B(–NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$), D(–NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$), E(–NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$), F(–NO$_2$, –NF$_2$, –N$_3$), and G(–NO$_2$, –ONO$_2$, –NF$_2$, –N$_3$) have smaller energy gaps than their corresponding unsubstituted molecules, reflecting a shift toward lower frequencies in their electronic absorption

Table 3 Calculated HOMO and LUMO energies (a.u.) and energy gaps ($\Delta E_{\text{LUMO–HOMO}}$) of the bridged di-1,3,5-triazines

	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{(LUMO–HOMO)}}$
A(−)			
A1	−0.2710	−0.0998	0.1713
A2	−0.2286	−0.0421	0.1865
A3	−0.3369	−0.1797	0.1572
A4	−0.3043	−0.1215	0.1828
A5	−0.3107	−0.1466	0.1641
A6	−0.2841	−0.1101	0.1740
B(−C−)			
B1	−0.2754	−0.0607	0.2148
B2	−0.2284	−0.0083	0.2201
B3	−0.3310	−0.1538	0.1772
B4	−0.3121	−0.1090	0.2031
B5	−0.3076	−0.1046	0.2030
B6	−0.2831	−0.0852	0.1979
D(−C−C−)			
D1	−0.2729	−0.0585	0.2144
D2	−0.2299	−0.0066	0.2233
D3	−0.3248	−0.1477	0.1771
D4	−0.3093	−0.1071	0.2022
D5	−0.3008	−0.1023	0.1984
D6	−0.2829	−0.0831	0.1998
F(−C=C−)			
F1	−0.2729	−0.1077	0.1652
F2	−0.2331	−0.0634	0.1697
F3	−0.3285	−0.1756	0.1529
F4	−0.2966	−0.1277	0.1689
F5	−0.3080	−0.1457	0.1623
F6	−0.2817	−0.1170	0.1646
C(−N−)			
C1	−0.2640	−0.0647	0.1993
C2	−0.2271	−0.0130	0.2141
C3	−0.3285	−0.1506	0.1778
C4	−0.2963	−0.1112	0.1851
C5	−0.3051	−0.1084	0.1967
C6	−0.2781	−0.0836	0.1945
E(−N−N−)			
E1	−0.2269	−0.0531	0.1738
E2	−0.1963	0.0081	0.2045
E3	−0.2935	−0.1488	0.1447
E4	−0.2538	−0.1110	0.1428
E5	−0.2675	−0.0970	0.1705
E6	−0.2391	−0.0785	0.1607
G(−N=N−)			
G1	−0.2653	−0.1190	0.1463
G2	−0.2249	−0.0722	0.1527
G3	−0.3257	−0.1890	0.1368
G4	−0.2849	−0.1371	0.1478
G5	−0.3021	−0.1606	0.1415
G6	−0.2717	−0.1237	0.1480

spectra. This shows that the effects of the substituents on the HOMO–LUMO gap are coupled to those of the bridge groups. Among the derivatives, D2 has the highest HOMO–LUMO gap, while G3 has the smallest one. Overall, comparing differently substituted bridged di-1,3,5-triazines leads to a comparison of the energetics. In addition, the CH2- and CH2–CH2-bridged di-1,3,5-triazines have larger HOMO–LUMO gaps than the corresponding substituted di-1,3,5-triazines with other bridging groups. Thus, we can infer that the CH2- and CH2–CH2-bridged ditriazines have relatively low reactivity compared to the other bridged derivatives.

Energetic properties

Detonation velocity and detonation pressure are two important performance parameters for an energetic material. Table 4 presents the calculated ρ, Q, D, P, and oxygen balance (OB) values of the bridged di-1,3,5-triazines, together with the corresponding experimental data [31]. For the sake of comparison, the experimental detonation performances of two known explosives, 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), are also listed in this table. As is evident from Table 4, the calculated densities of the bridged di-1,3,5-triazines agree well with the available experimental values. Although the error in or the limitations of the calculation method cause the predicted properties to deviate somewhat from the experimental values, these results are still reliable and meaningful.

Bridged di-1,3,5-triazines with different substituent groups have different ρ values; for example, the largest value and the smallest one are 2.07 and 1.39 g/cm^3, respectively. All of the substituted di-1,3,5-triazines have larger ρ values than their corresponding unsubstituted molecules. When the substituent is –NO2, –ONO2, or –NF2, the increase in the ρ value of the substituted di-1,3,5-triazine is fairly large compared with the corresponding unsubstituted molecule. The NF2-substituted di-1,3,5-triazine has the largest ρ value in the same series. When the bridge group is –CH2–, –CH2–CH2–, or –CH=CH–, the ρ values of the bridged di-1,3,5-triazines are smaller than those of the directly linked di-1,3,5-triazines (A) with the same substituents. The NH-, NH–NH-, and N=N-bridged di-1,3,5-triazines with –NH2 or –N3 have higher ρ values than those of the corresponding directly linked di-1,3,5-triazines (A), while the opposite is true of those with –NO2, –ONO2, or –NF2. This indicates that the effects of the bridges –NH–, –NH–NH–, and –N=N– on the ρ values are coupled to those of the substituents. It was also found that substituted di-1,3,5-triazines with the nitrogen bridge –NH– (–NH–NH– or –N=N–) have higher ρ values than the corresponding ones with the carbon bridge –CH2– (–CH2–CH2– or –CH=CH–). In addition, the substituted di-1,3,5-triazines with the conjugated bridge –CH=CH– have higher ρ

values than the corresponding ones with the unconjugated bridge –CH2–CH2–. Therefore, incorporating the substituent –NO2, –ONO2, or –NF2 into the directly linked di-1,3,5-triazine can greatly increase its ρ value.

The calculated heats of detonation in Table 4 show that substituting –NO2, –ONO2, –NF2, or –N3 increases the heat of detonation compared to that of the corresponding unsubstituted di-1,3,5-triazine, whereas the opposite is true for –NH2. Different bridge groups also have different effects on the heats of detonation of the bridged di-1,3,5-triazines. On the whole, –N=N– is an effective bridge for enhancing the heat of detonation of a bridged di-1,3,5-triazine.

The oxygen balance (OB) is a parameter that indicates the degree to which an explosive can be oxidized. OB is another important criterion for selecting potential HEDMs. Table 4 indicates that, by and large, the higher the oxygen balance, the larger the values of D and P, and the better the performance of the bridged di-1,3,5-triazine. However, it is clear that too much oxygen is not favorable for improving the explosive performance of an HEDM. The primary reason for this is that the additional oxygen will produce O2, which removes a great deal of the energy produced during the explosion of the high-energy material. Therefore, it is best to keep the oxygen balance at around zero when designing HEDMs. It can therefore be concluded that an –NO2 or –ONO2 group is a good substituent for improving the oxygen balance when designing potential HEDMs.

The effects of the substituents and/or bridges on the densities mean that the bridged di-1,3,-5-triazines have different D and P values. All of the substituted derivatives have larger D and P values than their unsubstituted equivalents, except for the derivatives with –NH2. It can be observed in Table 4 that the ρ values of A(–NO2, –ONO2, –NF2), B–NF2, C(–ONO2, –NF2), D–NF2, E(–ONO2, –NF2), F(–ONO2, –NF2), and G(–ONO2, –NF2) are very high: above 1.9 g/cm^3. Moreover, their D and P values are very high—close to or above 9.0 km/s and 39.0 GPa, respectively. This shows that an –ONO2 or –NF2 group is an effective structural unit for enhancing detonation properties. In addition, G–NF2, an N=N-bridged di-1,3,5-triazine with four –NF2 groups, has the largest D and P values among the derivatives. It was also found that the directly linked di-1,3,5-triazines and the N=N-bridged di-1,3,5-triazines have higher D and P values than the other derivatives with the same substituents. This indicates that the bridging group s –CH2–, –NH–, –CH2–CH2–, –NH–NH–, and –CH=CH– are unhelpful for increasing the detonation properties of the derivatives. Based on the above analyses, It can be concluded that an –ONO2, –NF2, or –N=N– group is an effective structural unit for increasing the densities and detonation properties of di-1,3,5-triazine derivatives.

Figure 3 displays the calculated ρ, D, and P values for the bridged di-1,3,5-triazines, together with those for the

Table 4 Predicted densities (G), heats of detonation (Q), detonation velocities (D), detonation pressures (P), and oxygen balance (OB) values for the bridged di-1,3,5-triazines [a]

Compound	V (cm³/mol)	Q (J/g)	OB [b]	ρ (g/cm³)	D (km/s)	P (GPa)
A(–)						
A1	106.11	965.70	−139.87	1.49	5.79	13.19
A2	142.88	432.57	−116.25	1.62	5.29	11.66
A3	176.10	1478.95	−18.81	1.85	8.31	31.18
A4	205.37	1491.52	0.00	1.92	8.82	35.43
A5	167.22	1530.27	−52.72	2.06	9.20	40.51
A6	189.14	1254.71	−59.22	1.68	7.17	21.89
B(–C–)						
B1	117.68	596.15	−156.16	1.45	4.98	9.59
B2	156.84	192.73	−129.78	1.56	3.38	4.63
B3	192.75	1410.10	−31.62	1.78	7.89	27.45
B4	220.56	1437.16	−11.48	1.82	8.28	30.60
B5	181.89	1467.34	−63.46	1.99	8.79	36.37
B6	203.42	1169.41	−70.95	1.63	6.93	20.03
C(–N–)						
C1	116.21	560.63	−132.44	1.51	5.15	10.49
C2	152.67	172.09	−112.22	1.59	3.25	4.33
C3	187.43	1375.87	−20.27	1.84	8.15	29.84
C4	213.18	1407.94	−1.91	1.90	8.61	33.95
C5	177.09	1435.09	−52.75	2.07	9.14	40.13
C6	196.79	1151.47	−58.95	1.71	7.19	22.21
D(–C–C–)						
D1	132.51	513.01	−170.03	1.39	4.64	8.10
D2	169.72	156.86	−141.78	1.53	2.48	2.46
D3	203.81	1355.81	−43.45	1.77	7.70	26.03
D4	231.17	1397.32	−22.21	1.80	8.09	29.10
D5	197.02	1420.37	−73.43	1.92	8.39	32.40
D6	215.11	1103.84	−81.75	1.60	6.77	18.90
E(–N–N–)						
E1	123.55	613.15	−126.19	1.54	5.54	12.32
E2	160.33	207.07	−108.69	1.58	3.89	6.17
E3	198.76	1352.25	−21.61	1.82	8.10	29.30
E4	221.16	1393.63	−3.68	1.88	9.26	38.98
E5	184.68	1414.20	−52.77	2.05	9.10	39.57
E6	203.74	1153.33	−58.71	1.70 (1.65[d])	7.30	22.87
F(–C=C–)						
F1	127.64	637.93	−163.28	1.44	4.88	9.14
F2	165.12	245.23	−136.44	1.52	3.89	6.01
F3	200.95	1403.19	−39.32	1.76	7.70	25.96
F4	226.36	1432.69	−18.60	1.82	8.14	29.58
F5	188.26	1460.60	−69.71	1.98	8.62	34.85
F6	211.08	1173.38	−77.65	1.62	6.77	19.05
G(–N=N–)						
G1	120.10	909.54	−119.04	1.55	6.05	14.76
G2	157.27	442.47	−103.12	1.68	5.50	12.86
G3	193.93	1521.75	−17.38	1.83	8.35	31.19
G4	221.18	1525.40	0.00	1.89	8.75	34.96
G5	184.89	1582.99	−48.96	2.03	9.26	40.82

Table 4 (continued)

Compound	V (cm^3/mol)	Q (J/g)	OB [b]	ρ (g/cm^3)	D (km/s)	P (GPa)
G6	204.29	1316.84	−54.51	1.71 (1.72[d])	7.39	23.39
RDX	124.91	1590.72	−21.61	1.780 (1.82[c])	8.87 (8.75[c])	34.67 (34.00[c])
HMX	157.50	1633.87	−21.61	1.880 (1.91[c])	9.28 (9.10[c])	39.19 (39.00[c])

[a] The average volumes were obtained from 100 single-point calculations performed at the B3LYP/6-31G(d,p) level

[b] Oxygen balance (%) for $C_aH_bO_cN_d$: $1{,}600 \times (c - 2a - b/2)/M_w$; M_w is the molecular weight of the compound

[c] The experimental values were taken from [1]

[d] The experimental values were taken from [31]

commonly used explosives RDX and HMX. It is clear that the trend in ρ throughout the series is very similar to the trends seen for D and P in the bridged di-1,3,5-triazines. However, some of the di-1,3,5-triazine derivatives have higher ρ values but lower D and P values than RDX or HMX. This is because their Q values cause ρ to have less influence on D and P. This in turn shows that density is not always the key factor when determining detonation properties. The derivatives A(–ONO$_2$, –NF$_2$), B–NF$_2$, C–NF$_2$, E(–ONO$_2$, –NF$_2$), F–NF$_2$, and G(–ONO$_2$, –NF$_2$) have D and P values comparable to those of RDX rather than HMX. However, only A–NF$_2$, C–NF$_2$, E–NF$_2$, and G–NF$_2$ gave better detonation performances (D and P) than HMX, one of the most widely used energetic ingredients of various high-performance explosives and propellant formulations. Although it is reported that E–N$_3$ and G–N$_3$ have been successfully synthesized, some of their detonation properties are still lacking. In addition, the syntheses of other energetic compounds have not yet been reported. If A–NF$_2$, B–NF$_2$, C–NF$_2$, E–NF$_2$, and G–NF$_2$ can be synthesized, they will have higher exploitable values. Thus, further investigations are still needed.

Thermal stability

The bond dissociation energy (BDE) provides useful information for understanding the stability of a molecule of interest. It should be pointed out that we selected relatively weak bonds in the compounds as the bonds that are broken, based on the bond order, when calculating the BDE. Also, the BDEs of relatively weak bonds in the bridges were calculated in order to evaluate the effects of different linkages on the stability of the derivatives. The Mulliken bond orders and BDEs of the weakest bonds in the di-1,3,5-triazine derivatives are listed in Table 5. It was found that the BDE value of the C–R bond is higher than that of the weak bonds in the bridges of the NH$_2$-substituted di-1,3,5-triazine derivatives, except for E–NH$_2$, while the opposite is true for the group –NO$_2$. In addition, attaching substituents increases the BDE values of the weak bonds in the bridges, except for the derivatives C–NH$_2$, D–NO$_2$, D–NF$_2$, E–NH$_2$, F–NH$_2$, F–N$_3$, G–NH$_2$, and G–N$_3$. Different bridge groups also have different effects on the BDEs for the bridged di-1,3,5-triazines. Compared with the directly linked di-1,3,5-triazines, some C–R bonds of the bridged molecules have

Fig. 3 Densities, detonation velocities, and detonation pressures of bridged di-1,3,5-triazines
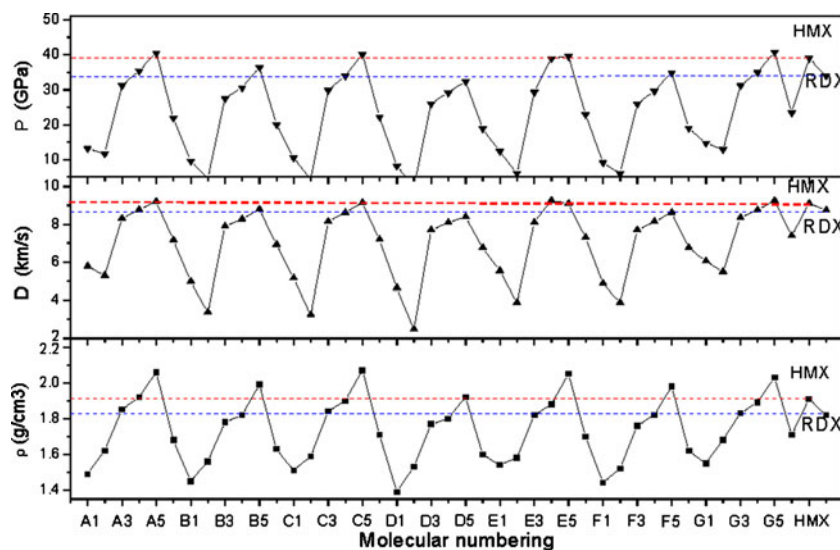
Table 5 Bond dissociation energies (BDE, kJ mol^{-1}) and Mulliken bond orders of the relatively weak bonds in the bridged di-1,3,5-triazines

Compound	C–R		C–C (bridge)		C–N (bridge)		N–N (bridge)		O–NO$_2$/N–F/N–N$_2$	
	P_{C-R}	BDE	P_{C-C}	BDE	P_{C-N}	BDE	P_{N-N}	BDE	$P_{N-R'}$	BDE
A(–)										
A1			0.2988	434.49						
A2	0.3207	475.48								
A3	0.1406	236.08								
A4	0.2327	379.84							0.1270 (O–NO$_2$)	168.90
A5	0.1577	268.55							0.1058 (N–F)	241.66
A6	0.2689	368.18							0.1987 (N–N$_2$)	752.47
B(–C–)										
B1			0.3469	362.95						
B2	0.3194	475.23	0.3464	368.27						
B3	0.1394	238.46	0.3463	370.39						
B4	0.2305	380.57	0.3475	375.06					0.1277 (O–NO$_2$)	139.49
B5	0.1561	269.23	0.3420	372.96					0.1050 (N–F)	242.38
B6	0.2676	368.34	0.3459	371.93					0.1998 (N–N$_2$)	752.67
C(–N–)										
C1					0.2602	447.80				
C2	0.3252	474.27			0.2555	436.55				
C3	0.1434	237.81			0.2594	463.44				
C4	0.2333	378.98			0.2580	459.05			0.1286 (O–NO$_2$)	146.16
C5	0.1599	269.37			0.2547	460.67			0.1050 (N–F)	243.20
C6	0.2729	365.65			0.2538	453.51			0.1988 (N–N$_2$)	750.90
D(–C–C–)										
D1					0.3286	286.43				
D2	0.3173	474.68			0.3494	296.61				
D3	0.1367	239.93			0.3006	279.97				
D4	0.2242	381.70			0.3500	289.89			0.1286 (O–NO$_2$)	136.89
D5	0.1522	267.64			0.3326	284.18			0.1038 (N–F)	241.87
D6	0.2650	367.48			0.3473	289.20			0.1994 (N–N$_2$)	751.17
E(–N–N–)										
E1							0.1780	306.64		
E2	0.3243	473.06					0.2013	297.99		
E3	0.1406	241.03					0.1867	327.48		
E4	0.2296	380.42					0.1817	323.68	0.1289 (O–NO$_2$)	142.80
E5	0.1600	271.26					0.1815	325.46	0.1035 (N–F)	244.19
E6	0.2708	366.22					0.1801	314.53	0.2046 (N–N$_2$)	751.13
F(–C=C–)										
F1			0.3701	489.02						
F2	0.3211	475.45	0.3654	481.04						
F3	0.1393	238.45	0.3790	494.10						
F4	0.2295	378.61	0.3744	491.20					0.1276 (O–NO$_2$)	144.44
F5	0.1556	269.38	0.3711	493.35					0.1043 (N–F)	242.27
F6	0.2668	365.00	0.3720	488.62					0.2016 (N–N$_2$)	751.06
G(–N=N–)										
G1					0.2494	254.31				
G2	0.3273	480.09			0.2455	245.56				
G3	0.1415	235.22			0.2395	258.39				
G4	0.2367	381.34			0.2402	257.84			0.1265 (O–NO$_2$)	140.42

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Table 5 (continued)

Compound	C–R		C–C (bridge)		C–N (bridge)		N–N (bridge)		O–NO$_2$/N–F/N–N$_2$	
	P_{C-R}	BDE	P_{C-C}	BDE	P_{C-N}	BDE	P_{N-N}	BDE	$P_{N-R'}$	BDE
G5	0.1592	256.71			0.2377	259.53			0.1061 (N–F)	256.71
G6	0.2725	370.40			0.2462	254.20			0.1989 (N–N$_2$)	753.34
RDX	0.1672	172.62								
HMX	0.1701	182.31								

higher BDEs, while others have smaller BDEs due to the presence of different substituents. None of the bridge groups had a dominant influence on the BDEs of the C–R bonds.

It was also found that the O–NO$_2$ or N–F bonds in the ONO$_2$- or NF$_2$-substituted bridged di-1,3,5-triazines had smaller BDE values than the other bonds in the same molecule, when the O–NO$_2$ or N–F bonds had slightly different BDEs when different linkage groups were incorporated. The calculated BDE can be used to gauge the order of thermal stability for a group of energetic materials [60]. Therefore, we can infer that the trigger bond is O–NO$_2$ or N–F in the ONO$_2$- or NF$_2$-substituted bridged di-1,3,5-triazines. By examining the calculated BDE and bond orders, we can deduce that ring or bridge cleavage is difficult during thermal decomposition. C–R homolysis is also not easy, because the C–R bond has a higher BDE. Compared with the important modern explosives RDX and HMX, most of the bridged di-1,3,5-triazines have higher BDEs for their weakest bonds. This indicates that most of them have high thermal stabilities, in agreement with previous experimental reports [31].

It is interesting to note that the C–NH$_2$ bond in B–NH$_2$ has a higher BDE than the C–C bond in the bridge of B–NH$_2$, whereas the former has a lower bond order than the latter. The same is true of B–ONO$_2$, C–N$_3$, D–NH$_2$, D–ONO$_2$, D–N$_3$, and G–ONO$_2$. This indicates that the trend in BDE with different substituents and bridges is inconsistent with that of the bond order for some relatively weak bonds. A similar situation was also found to occur for other bonds. The N–N$_2$ bond in A–N$_3$, B–N$_3$, C–N$_3$, D–N$_3$, E–N$_3$, F–N$_3$, or G–N$_3$ has a higher BDE than its C–N$_3$ bond, whereas the former has a lower bond order than the latter. Therefore, we cannot judge the thermal stability of the di-1,3,5-triazine derivatives solely based on the bond order; it is necessary to consider the BDE.

Figure 4 presents the BDEs of the weakest bonds for the bridged di-1,3,5-triazine derivatives along with RDX and HMX. The BDE value of E–N$_3$ (314.53 kJ mol^{-1}) is higher than that of G–N$_3$ (254.20 kJ mol^{-1}). This shows that E–N$_3$ has better thermal stability than G–N$_3$. In fact, the decomposition of E–N$_3$ occurs at ca. 202 °C [31], whereas that of G–N$_3$ takes place at about 200 °C [31]. Also, the impact

sensitivity of E–N$_3$ (H_{50}=18.3 cm [31], where H_{50} is the height from which the sample is impacted by a hammer and there is a 50% probability of causing an explosion; i.e., the lower H_{50}, the more sensitive the explosive) is threefold less than that of G–N$_3$ (H_{50}=6.2 cm) [31]. These experimental observations support the conclusion we drew from the BDE values. It is also clear from Fig. 4 that most of the weakest bonds in the bridged di-1,3,5-triazines have a relatively high BDE values. Compared with the commonly used explosives RDX and HMX, most of the bridged di-1,3,5-triazine derivatives have higher BDE values, except for the derivatives with the group –ONO$_2$. In particular, F–H has the highest BDE value of 489.02 kJ mol^{-1} among the weakest bonds of the bridged di-1,3,5-triazines. On the whole, an –NH$_2$, –N$_3$, –NH–, or –CH=CH– group is an effective structural unit for enhancing the thermal stability of the derivative.

As is well known, a good nitrogen-rich HEDM candidate not only has excellent detonation properties but could also exist stably. Considering the detonation performance and thermal stability, it can be concluded that A(–ONO$_2$, –NF$_2$), B–NF$_2$, C–NF$_2$, E(–ONO$_2$, –NF$_2$), F–NF$_2$, and G(–ONO$_2$, –NF$_2$) possess better detonation performances (D and P) and thermal stabilities (BDE) than RDX. Therefore, these nine compounds can be considered as potential
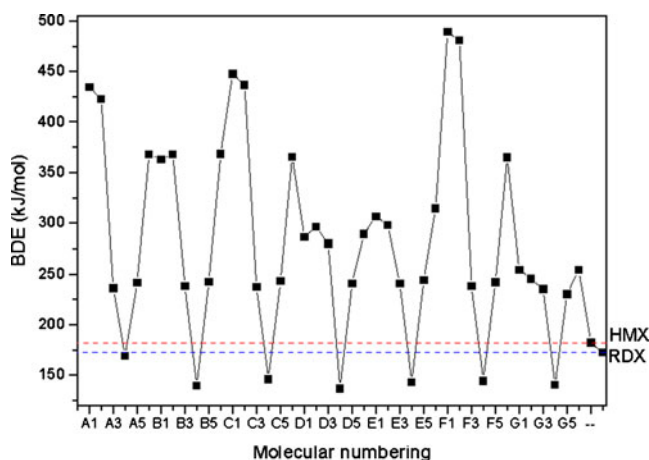
Fig. 4 Bond dissociation energies of the weakest bonds for the bridged di-1,3,5-triazines

candidates for HEDMs with enhanced performance and reduced sensitivity.

Conclusions

In this work, we have studied the HOFs, electronic structures, energetic properties, and thermal stabilities of a series of bridged di-1,3,5-triazine derivatives with different linkages and substituents using the DFT-B3LYP method. The results show that an $-N_3$ or $-N=N-$ group is an effective structural unit for increasing the HOF values of the derivatives. Substitution of the $-NH_2$ group increases the HOMO and LUMO energies, whereas attaching $-NO_2$, $-ONO_2$, $-NF_2$, or $-N_3$ decreases them. The effects of substituents on the HOMO–LUMO gap combine with those of the bridge groups.

The calculated detonation velocities and detonation pressures of the derivatives indicate that substituting the $-ONO_2$, $-NF_2$, or $-N=N-$ group is very useful for enhancing detonation performance. An analysis of the bond dissociation energies for several relatively weak bonds suggests that most of the derivatives have good thermal stabilities. Cleavage of the ring or bridge during thermal decomposition is unlikely. On the whole, an $-NH_2$, $-N_3$, $-NH-$, or $-CH=CH-$ group is an effective structural unit for enhancing the thermal stability of the derivatives. Considering their detonation performances and thermal stabilities, A($-ONO_2$, $-NF_2$), B$-NF_2$, C$-NF_2$, E($-ONO_2$, $-NF_2$), F$-NF_2$, and G($-ONO_2$, $-NF_2$) may be considered potential candidates for HEDMs with enhanced performance and reduced sensitivity. These results provide basic information that should prove useful in the molecular design of novel HEDMs.

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