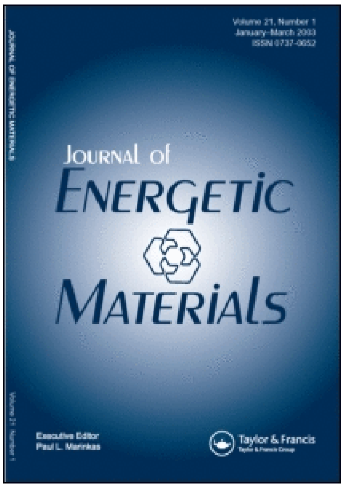

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Theoretical Study of 2,4,6-Tris(3′,5′-Diamino-2′,4′,6′-Trinitrophenylamino)-1,3,5-Triazine

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The density functional theory (DFT) BLYP and B3LYP method with 3–21G* and 6–31G** basis sets were used to predict the structures, natural bond orbital (NBO) atomic charges, and ring interactions of 2,4,6-tris(3′,5′-diamino-2′,4′,6′-trinitrophenylamino)-1,3,5-triazine (PL-1). Approximately, the molecule possesses C_3 symmetry with three benzene rings tilted to the triazine plane. The interactions among three 3′,5′-diamino-2′,4′,6′-trinitrophenylamino groups are of additivity. The heat of formation of PL-1 was estimated to be 427.6 J/mol via isodesmic reaction. Detonation velocity and pressure are 8.5 km/s and 35.5 GPa, respectively.

Keywords: 2,4,6-tris(3′,5′-diamino-2′,4′,6′-trinitrophenylamino)-1,3,5-triazine (PL-1), detonation velocity and pressure, DFT calculation, heat of formation, ring interaction

Introduction

Theoretical treatment of energetic molecules receives a wide range of recognition since it provides the necessary data needed

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for predicting the structures, thermodynamic properties, spectroscopy, bonding characteristics, and so on [1–9]. This information will be helpful for further investigation as well as molecular design of energetic compounds. 2,4,6-Tris(3′,5′-diamino-2′,4′,6′-trinitrophenylamino)-1,3,5-triazine (PL-1; Fig. 1) is a new thermally stable and insensitive explosive. The thermal stability and performance of PL-1 is slightly inferior to TATB, but its density is better than TATB. In addition to impact and friction is comparable with TATB [10,11]. The attention this molecule has received has to do not only with its applications but also with its intriguing symmetry and electronic withdraw–donate groups. In addition, the lone pair electrons on the nitrogen atoms of the amino and nitro groups are coplanar with π bonds of six-numbered rings, which provides a possible

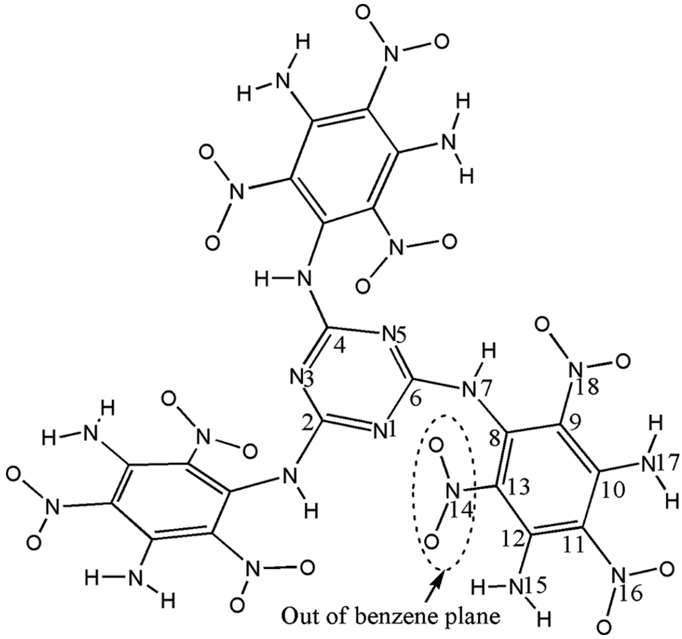
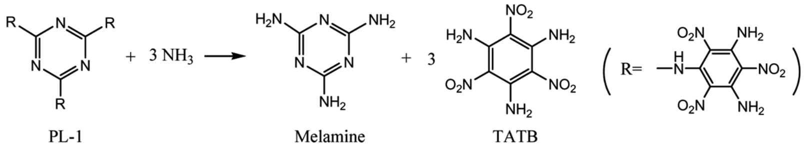


Figure 1. Molecular structure and some atomic numbering of PL-1.

low-energy channel for the insulator-to-metal transition and causes the bending of PL-1 nitro groups to be more difficult than that of nitromethane. What is the total energy of the interactions between the substituted benzene rings in PL-1? How much do the conjugation effects contribute to stabilization? Are the benzene rings constrained in their rotations with respect to triazine and with what energy barriers in rotating? As far as we know, there has not been such theoretical investigation on PL-1. In this article, we performed full optimization on PL-1 by DFT method with B3LYP and BLYP functionals [12,13]. Based on the optimized structure, thermodynamic properties were obtained. We also predicted the detonation pressure and velocity.

Computational Methods

The title molecule obtained from Chem3D software was fully optimized at the DFT-B3LYP and BLYP levels by the Berny method [14,15] with 3–21G* and 6–31G** basis sets. Frequency calculations were performed on each optimized structure. Natural bond orbital analyses and computations of electron density at bonding critical points were performed at the B3LYP/3–21G* level, since these properties are not sensitive to the basis sets. The computed frequencies were used to derive the thermodynamic functions heat capacity, thermal corrections for enthalpy, and entropy employing the statistical thermodynamic method. The heat of formation (ΔH_f) of PL-1 was evaluated from the following isodesmic reaction by Eq. (1).



$$\begin{aligned} \Delta H^o_{298} &= \Delta E_0 + \Delta ZPE + \Delta(H^o_{298} - H^o_0) \\ &= \Sigma\Delta H_f(\mathrm{P}) - \Sigma\Delta H_f(\mathrm{R}) \end{aligned} \tag{1}$$

where the ΔH^o_{298} is the enthalpy change of the reaction at 298 K. $\Delta E_0, \Delta ZPE$, and $\Delta(H^o_{298} - \Delta H^o_{290})$ are the changes in the total energy, the zero point energy, and the enthalpy change from 0 K to 298 K, respectively. $\Sigma\Delta H_f(P)$ and $\Sigma\Delta H_f(R)$ are the sums of the heats of formation of the products and reactants, respectively. The evaluation of the standard thermodynamic functions was carried out using a self-programmed code based on the theory of classical statistical thermodynamics [16]. Geometry optimizations and vibrational analyses were carried out with the Gaussian 98 code with the default convergence cutoffs given in the program [17]. The evaluation of electron density is derived from the AIM2000 program [18]. The detonation velocity (D) and detonation pressure (P) were calculated by using empirical Kamlet-Jacobs equations [19].

Results and Discussion

Optimized Geometries

The fully optimized structure of PL-1 is shown in Fig. 1. Approximately, the molecule possesses C_3 symmetry with three benzene rings tilted to the triazine plane. All three benzene rings are geometrically the same and look like screw propellers that are evenly attached to the center triazine plane via a secondary amino group. Table 1 lists parts of geometrical parameters that related to the triazine ring and one of the benzene rings. The geometries of the other two benzene rings and their substituted groups are very similar to those listed.

As can be seen from Table 1, large basis set produces slightly large bond lengths, while bond lengths obtained from B3LYP are slightly shorter than those from BLYP. The values of dihedral angles from all four computational levels show that a tilt angle of ca. 30° between the planes of the benzene and triazine, providing only partial conjugations between the center and outer rings. Since the geometrical parameters at the B3LYP/6–31G** level are somewhat intermediate compared to those obtained from other computational levels and also since the average errors of geometries from B3LYP/6–31G**

Table 1
Selected geometrical parameters of PL-1 at different computational levels

Parameters	BLYP/3–21G*	BLYP/6–31G**	B3LYP/3–21G*	B3LYP/6–31G**
$R_{\mathrm{C-NH2}}$	1.3365–1.3375	1.3405–1.3415	1.3245–1.3255	1.3305
$R_{\mathrm{C6-N7}}$	1.3905	1.3925	1.3765	1.3795
$R_{\mathrm{N7-C8}}$	1.3735	1.3815	1.3645	1.3745
$R_{\mathrm{C-N(nitro)}}$	1.4345–1.4565	1.4475–1.4715	1.4185–1.4415	1.4355–1.4595
$D_{1\text{–}6\text{–}7\text{–}8}$	−11.3	1.0	−5.7	0.9
$D_{6\text{–}7\text{–}8\text{–}13}$	−25.3	−32.2	−25.3	−34.6

are relatively small [20], the remaining discussion associated with the geometries will focus on the results from the B3LYP/6–31G** level. The C—NO_2 bonds are lengthier than the other type of C—N bonds. The oxygen atoms of the nitro group next to the triazine are out of the benzene ring to which it attaches (Fig. 1), which lowers the conjugation between this nitro group and benzene ring. As a result, the C_{13}—N_{14} bond is slightly lengthier than those of C_9—N_{18} and C_{11}—N_{16} and thus is prone to rupture upon stimuli.

NBO Charges, Electron Densities (ρ) at Bonding Critical Points

Table 2 lists the NBO charges for PL-1 at the B3LYP/3–21G* level. The NBO theory applies an interatomic orthogonalization step to establish asymmetrical atomic orbitals [21] and thus gives charges of relatively basis-set independence compared to other methods such as Mulliken charges and its variations. As can be seen from Table 2, N_{15} and N_{17} atoms carry large negative charges since their pyramid structure of

Table 2
NBO charges of PL-1 at the B3LYP/3–21G* level

Atoms	Charges	Atoms	Charges
N_1	−0.5373	C_{11}	−0.0172
C_2	0.6271	C_{12}	0.2435
N_3	−0.5371	C_{13}	−0.0120
C_4	0.6271	N_{14}	0.3682
N_5	−0.5369	N_{15}	−0.7203
C_6	0.6270	N_{16}	0.3441
N_7	−0.5752	N_{17}	−0.7188
C_8	0.2565	N_{18}	0.3389
C_9	−.0.0037	O^a	−0.2832
C_{10}	0.2398	O	−0.34 to −0.35

[a] Nitro oxygen atoms that are out of the benzene ring (see Fig. 1).

amino groups make them weakly conjugated with benzene ring and unable to share the nitrogen lone pair, while all the carbon atoms on the triazine bear large positive charges due to the electronic pulling effects of their neighbor nitrogen atoms. These large charge separations between neighbor atoms facilitate a heterolytic cleavage of the relevant bonds. Also notable is that one nitro oxygen atom, which is out of the benzene plane, bears much less negative charges (-0.2832) than those (in range of -0.3434 to -0.3494) of all the other nitro oxygen atoms, since the former is not conjugated with the benzene ring and unable to withdraw the electron from the benzene ring.

Table 3 also reports the electron density at bonding critical points. The evaluation of electron density is derived from the AIM2000 program. The atoms in molecules (AIM) theory of Bader [18] defines a discrete rather then a fuzzy boundary on which space partitioning can be based. The electron densities from the AIM theory are not sensitive to either the basis set or induction of the electron correlation. As can be seen from Table 3, the $C-NO_2$ bonds are the weakest, followed by N_7-C_6/C_8 bonds, indicating that the $C-NO_2$ is prone to rupture in an initial decomposition process. Electron densities at bonding critical points on the aromatic rings, which are not collected, are much larger than those listed in Table 3, indicating that there exists a conjugating effect within the ring and that the bond strengths are much larger than that of a single bond.

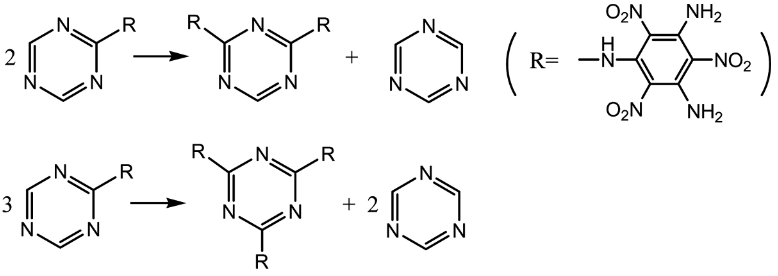
Table 3

Electron densities (ρ) at bonding critical points at the B3LYP/3−21G* level

Bond	ρ	Bond	ρ
C_6-N_7	0.2860	C_9-N_{18}	0.2496
N_7-C_8	0.2920	$C_{11}-N_{16}$	0.2499
N_7-H	0.2842	$C_{12}-N_{15}$	0.3225
$C_{13}-N_{14}$	0.2423	$C_{10}-N_{17}$	0.3226

Ring Interactions

To evaluate the conjugations of triazine and benzene rings being connected via imino group, single point energies were calculated when the planes of these two rings were placed vertical by the internal rotations of C_6—N_7 or N_7—C_8. The total energies of PL-1 thus obtained are 96.4 and 94.9 less stable than the most stable conformer, respectively, when the dihedral angles of $D_{1\text{–}6\text{–}7\text{–}8}$ and $D_{6\text{–}7\text{–}8\text{–}9}$ equal 90°. The energy differences demonstrate the conjugation effects between triazine and benzene rings. To estimate the interactions among substituted benzene rings attached to the triazine, we computed the disproportionation energy [22] at the B3LYP/3–21G* level, according to the energy change of the isodesmic reaction:



The disproportionation energies $E_{\text{disproportion}}$ of di- and tris-substituted triazines are 3.5 and 10.1 kJ/mol, indicating that the interactions among 3′,5′-diamino-2′,4′,6′-trinitrophenylamino groups being attached to triazine are small. Since 3×3.5 is approximately equivalent to 10.1, the interactions among three 3′,5′-diamino-2′,4′,6′-trinitrophenylamino groups are of additivity.

Heat of Formation, Detonation Velocity, and Pressure

Table 4 lists the total energies, zero-point energies, and the values of thermal correction at the B3LYP/6–31G* levels for

Table 4

Calculated total energy (E_0), zero-point energy (*ZPE*), values of thermal correction to enthalpy (H_T), and heats of formation (*HOF*) of the reference compounds and PL-1 at the B3LYP/6–31G** level[a]

Compd.	E_0	*ZPE*	H_T	*HOF*
NH_3	−56.5577682	88.62	10.01	−46.13 [27]
Melamine	−446.5119969	299.81	24.93	−51.9 [27]
TATB	−1011.8564920	408.90	42.51	28.5 [25]
PL-1	−3312.3098792	1242.82	137.79	427.6[b]

[a] E_0 is in a.u., *ZPE*, *HOF*, and H_T are in kJ/mol. The scaling factor for *ZPE* and H_T is 0.96 [28]. HOFs of melamine as well as TATB are from the sum of heat of formation at 298.15 K in the solid phase and the enthalpy of sublimation.

[b] This work.

three reference compounds being enlisted in the isodesmic reaction (1). The predicted HOF of PL-1, together with the total energies, zero-point energies, and the values of thermal correction are also summarized in Table 4. Previous studies have shown that the theoretically predicted values of HOF were in good agreement with experiments by choosing appropriate reference compounds in the isodesmic reaction [23,24].

On the basis of the estimated value of HOF, the detonation velocity (D) and pressure (P) of PL-1 are 8.5 km/s and 35.5 GPa, respectively. These values are not as high as some well-known widely used explosives such as HMX ($D = 9.1$ km/s, $P = 39.5$ GPa [25]). However, the D and P are expected to increase dramatically when PL-1 is binded with oxidizers, as in the practical cases of mixture explosives, since the title compound is in deficient of oxygen atoms. In addition, the peripheral electronic withdraw–donate groups of PL-1 enable it to bind well with polymers to form polymer-bonded explosives (PBXs) with good mechanical properties. Therefore, PL-1 is expected to be novel candidate of high energetic density materials (HEDM).

Conclusions

All three benzene rings are geometrically alike as screw propellers that are evenly attached to the center triazine plane by the connection of an amino group. There is a tilt angle of ca. 30° between the planes of the benzene ring and the triazine plane, providing only partial conjugations between the center and outer rings. The nitro group next to the triazine is out of the benzene ring to which it attaches, resulting in the $C{-}NO_2$ bond being the lengthiest and the weakest. The interactions among 3′,5′-diamino-2′,4′,6′-trinitrophenylamino groups attached to triazine are small and additive. Detonation velocity (D) and pressure (P) of PL-1 are 8.5 km/s and 35.5 GPa, respectively. These values are somewhere in between HMX ($D = 9.1$ km/s, $P = 39.5$ GPa) and TATB ($D = 7.6$ km/s, $P = 30$ GPa) [25,26] in terms of detonation performance.

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