Quantum Chemical Study of Aminonitrocyclopentanes as Possible High Energy Density Materials (HEDMs)

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Abstract: Nitro and amine groups were introduced into the cyclopentane skeleton, and the heats of formation, detonation performance, bond dissociation energies, and impact sensitivity for these aminonitrocyclopentanes were calculated in detail at the B3LYP/6-311G** level. The results show that all of the derivatives have negative heats of formation, which are influenced by the position of the substituent groups. Their stabilities were estimated and analyzed according to their bond dissociation energies and calculated characteristic H_{50} values. Most of the compounds were found to have a lower impact sensitivity than HMX. Furthermore, the detonation velocities and detonation pressures were predicted via the Kamlet-Jacobs equation. Of all these aminonitrocyclopentanes, E has the best detonation properties (ρ = 2.05 g/cm^3, D = 9.11 m/s, P = 39.62 GPa) and can be considered as a candidate high energy density material.

Keywords: cyclopentane derivatives, high energy density materials, impact sensitivity, quantum chemistry, DFT, available free space

Introduction

Energetic materials are extensively used for a variety of military purposes and industrial applications. The search for new materials is ongoing [1-9], and good

energetic materials have certain desirable physical and chemical characteristics: good oxygen balance, high thermal stability, high energy, and low sensitivity [10-12]. Current interest has been focused on the development of high-energy-density materials (HEDMs), with higher performance and/or decreased sensitivity to thermal and mechanical shock and friction [13-15]. However, the requirements of insensitivity and high energy often conflict, making the development of new HEDMs a difficult and challenging problem [16].

Since the original isolation of 1,3,5-triamino-2,4,6-trinitrobenzene (known as TATB) and 1,1-diamino-2,2-dinitroethylene (known as FOX-7) in 1888 and 1998 [17], respectively, there have been abundant experimental and theoretical studies on HEDMs. It is readily recognized that intermolecular hydrogen bonding in the solid phase makes a positive contribution to the efficacy of HEDMs [18]. The unit cell of TATB in particular consists of molecules arranged in planar sheets. These sheets are held together by strong intra- and inter-molecular hydrogen bonding, resulting in a graphite-like lattice structure with lubricating and elastic properties. So, we were inspired to design new high energy molecules possessing hydrogen bonding. In practice, new energetic compounds are often designed by modifying known substances with high densities by the addition and/or modification of explosophoric groups in the parent molecules. In our present work, cyclopentane was selected as the parent molecule, and nitro and amine groups were introduced to the cyclopentane skeleton. The geometries, thermodynamic properties, and stabilities of these aminonitrocyclopentanes were analysed, and their detonation performances were evaluated. The results of this study may provide some useful information in the search for novel energetic materials.

Theoretical Methods

The geometries of the aminonitrocyclopentanes were fully optimized at the DFT-B3LYP/6-311G** level with the Gaussian 03 program package, and harmonic vibrational analyses were performed subsequently on each optimized structure at the same level. The molecular frameworks of a series of the aminonitrocyclopentanes, designated A (1-amino-1-nitrocyclopentane), B1 (cis-1,2-diamino-1,2-dinitrocyclope ntane), B2 (cis-1,3-diamino-1,3-dinitrocyclopentane), C1 (cis,cis-1,2,3-triamino-1,2,3 -trinitrocyclopentane), C2 (cis,cis-1,2,4-triamino-1,2,4-trinitrocyclopentane), D (cis,cis,cis-1,2,3,4-tetraamino-1,2,3,4-tetranitrocyclopentane), and E (cis,cis,cis,cis-1,2,3,4,5-pentaamino-1,2,3,4,5-pentanitrocyclopentane), are displayed in Figure 1.
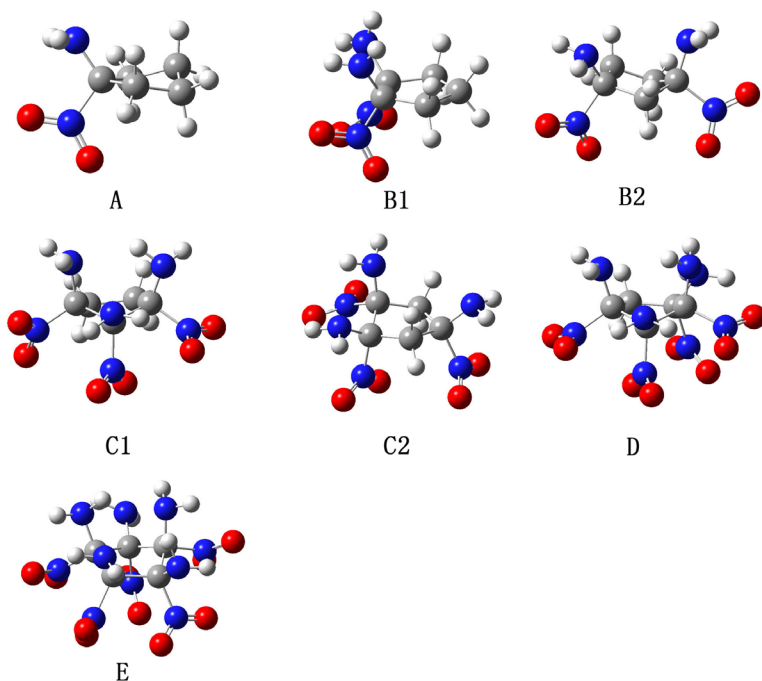
Figure 1. Optimized geometry for the aminonitrocyclopentanes studied.
A: 1-amino-1-nitrocyclopentane
B1: cis-1,2-diamino-1,2-dinitrocyclopentane
B2: cis-1,3-diamino-1,3-dinitrocyclopentane
C1: cis,cis-1,2,3-triamino-1,2,3-trinitrocyclopentane
C2: cis,cis-1,2,4-triamino-1,2,4-trinitrocyclopentane
D: cis,cis,cis-1,2,3,4-tetraamino-1,2,3,4-tetranitrocyclopentane
E: cis,cis,cis,cis-1,2,3,4,5-pentaamino-1,2,3,4,5-pentanitrocyclo-pentane

The heats of formation (HOF) of the various aminonitrocyclopentane molecules were determined using the gas-phase isodesmic reaction [19, 20].

$$C_5H_{10-2n}(NH_2)_n(NO_2)_n + 2nCH_4 \rightarrow C_5H_{10} + nCH_3NH_2 + nCH_3NO_2 \quad (1)$$

For reaction (1), the heat of reaction (ΔH_{298}) can be calculated from the following equation (2).

$$\Delta H_{298} = \Delta H_{f,\,p} - \Delta H_{f,\,R} \tag{2}$$

where $\Delta H_{f,\,p}$ and $\Delta H_{f,\,R}$ are the HOFs of the products and reactants at 298 K, respectively. The experimental HOFs of the reference compounds CH_4, C_5H_{10}, CH_3NH_2, and CH_3NO_2 are available, and were obtained from the NIST WebBook. Thus, the HOFs of the aminonitrocyclopentanes can be calculated once ΔH_{298} is known. The ΔH_{298} can be calculated using the following formula (3).

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT \tag{3}$$

Detonation performance is an important factor and must be considered when designing HEDMs. The semi-empirical Kamlet-Jacobs equation [21] was applied in previous work. The formulae (4) and (5) were listed as follows:

$$D = 1.01(N\overline{M}^{1/2}\,Q^{1/2})^{1/2}\,(1+1.03\rho_0) \tag{4}$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}\,Q^{1/2} \tag{5}$$

D is the detonation velocity (km s^{-1}), P is the detonation pressure (GPa), N is the moles of gas produced per gram of explosive, and $\overline{M}$ is the mean molecular weight of the gaseous detonation products. Q is the heat of detonation (cal g^{-1}), ρ_0 is the theoretical molecular density (g cm^{-3}), which was calculated from the molar weight (M) divided by the average molar volume (V), which in turn was gained from the arithmetic average value of 100 single point molar volumes, defined as the volume of 0.001 electron Bohr^{-3} electron density envelope and computed by Monte Carlo integration.

However the procedure used to estimate densities can lead to significant errors. Politzer *et al.* considered that the solid density can be corrected by the electrostatic potential [22, 23]. The method utilizes equations (6)-(10).

$$\text{Crystal density } (\rho_0) = \alpha\,(M/Vm) + \beta\,(\nu\sigma^2_{tot}) + \gamma \tag{6}$$

$$\sigma^2_{tot} = \sigma^2_+ + \sigma^2_- = \frac{1}{m}\sum_{i=1}^{m}[V^+(r_i) - \overline{V}_s^+]^2 + \frac{1}{n}\sum_{j=1}^{n}[V^-(r_j) - \overline{V}_s^-]^2 \tag{7}$$

$$\nu = \sigma^2_+\,\sigma^2_- / |\sigma^2_{tot}|^2 \tag{8}$$

$$V_S^+ = \frac{1}{m}\sum_{i=1}^{m}V^+(r_i) \tag{9}$$

$$V_S^- = \frac{1}{n}\sum_{j=1}^{n} V^-(r_j) \tag{10}$$

where: ν is the balance parameter, $V(r)$ is the electrostatic potential, $V(r_i)$ is the value of $V(r)$ at any point r_i on the surface, $V_S^+(r_i)$ and $V_S^-(r_j)$ represent the positive and negative values of $V(r)$ on the surface. $\overline{V_S^+}$ and $\overline{V_S^-}$ are their average values, and σ_{tot}^2 is the total variance. In the present paper, these parameter for the title compounds were obtained at the B3LYP/6-311G** level.

The strength of bonding is fundamental to understanding chemical processes and is evaluated by BDEs. The homolysis reaction of A-B is used to calculate the BDEs:

$$A - B(g) \rightarrow A^{\bullet}(g) + B^{\bullet}(g) \tag{11}$$

$$BDE_{(A-B)} = [E_{A\bullet} + E_{B\bullet}] - E_{(A-B)} \tag{12}$$

The bond dissociation energy, with zero-point energy (ZPE) correction, can be calculated using equation (13):

$$BDE_{(A-B)ZPE} = [E_{A\bullet} + E_{B\bullet}] - E_{(A-B)} + \Delta ZPE \tag{13}$$

$BDE_{(A-B)}$ is the BDE of the bond A-B, and $E_{(A-B)}$, $E_{A\bullet}$ and $E_{B\bullet}$ are the total energies of the parent molecule and the corresponding radicals, respectively.

The impact sensitivity, usually expressed as the impact sensitivity index (*i.e.*, characteristic height $-$ H_{50}), is one of the quantities used to scale the reliable performance of energetic materials. It is usually measured by the drop-weight impact test. The characteristic height was estimated using Eq. (14) as suggested by Cao [24]:

$$H_{50} = 0.1926 + 98.64 Q_{NO2}^2 - 0.03405 OB_{100} \tag{14}$$

Q_{NO2} is the net charge of the nitro group, and OB_{100} is the oxygen balance.

Another method for obtaining the characteristic height was proposed by Pospíšil *et al.* [25]:

$$H_{50} = \alpha_2 \sigma_+^2 + \beta_2 \gamma + \lambda_2 \tag{15}$$

where the values of the coefficients are taken from Ref. [25].

Results and Discussion

Heats of formation (HOF)

HOF is one of the most important thermochemical properties of energetic materials because it is related directly to the detonation parameters. The HOF is frequently taken to be indicative of their 'energetic content'. The method of isodesmic reactions has been employed very successfully to calculate HOFs. In an isodesmic reaction, the number of each kind of formal bond is conserved, and must comply with the bond separation reaction (BSR) rules. The total energies, the zero-point energies, the values of the thermal correction, and HOFs at the B3LYP/6-311G** level are listed in Table 1. By inspecting the HOFs in Table 1, it was found that all compounds have negative HOFs. However, the changes in the HOFs did not meet the group additivity rule when two groups were introduced into the cyclopentane skeleton, and these may be affected by intramolecular hydrogen bonding. Moreover, it is noteworthy that the HOFs of aminonitrocyclopentane isomers, with the same number of substituent groups, are affected by the relative positions of the nitro and amine groups. For C1 and C2, the HOF of C1 is higher (less negative) than that of C2, which indicates that an aminonitrocyclopentane is more stable when the substituent groups are kept far away from each other.

Table 1.   Calculated total energies (E_0, a.u.), zero-point energies (ZPE, a.u.), values of the thermal correction (H_T, a.u.), and HOFs (kJ/mol) at the B3LYP-6-311G** level

Compound	E_0	ZPE	H_T	HOF
A	-456.54414	0.16021	0.00956	-206.59
B1	-716.45887	0.17951	0.01324	-276.12
B2	-716.47139	0.17948	0.01341	-308.62
C1	-976.37754	0.19852	0.01703	-356.46
C2	-976.38732	0.19865	0.01702	-381.83
D	-1236.28491	0.21781	0.02048	-407.30
E	-1496.16315	0.23708	0.02357	-382.65

Detonation performance

The detonation velocity (D) and detonation pressure (P) are two important performance parameters for an energetic material. Several empirical methods have been applied to estimate these parameters. The Kamlet-Jacobs approach has proved to be reliable [26]. The theoretical molecular density (ρ), the corrected density (ρ_0), the heat of detonation (Q), the detonation velocity (D)

and the detonation pressure (P) are listed in Table 2. For a comparison, the experimental detonation parameters of two well-known explosives RDX and HMX are also listed.

Table 2. Calculated molecular density (ρ_0, g/cm^3), heat of detonation (Q, cal/g), detonation velocity (D, km/s) and detonation pressure (P, GPa) for the aminonitrocyclopentanes, together with RDX and HMX at the B3LYP/6-311G** level

Compound	ρ	ρ_0	Q	D	P
A	1.30	1.31	509.42	5.15	9.51
B1	1.61	1.63	869.51	6.84	19.53
B2	1.51	1.53	828.64	6.47	16.73
C1	1.68	1.70	1379.52	7.99	27.34
C2	1.68	1.68	1355.27	7.90	26.57
D	1.80	1.81	1225.02	8.30	30.61
E	2.06	2.05	1169.38	9.11	39.62
RDX	1.78(1.82)		1591.03	8.87(8.75)	34.67(34.00)
HMX	1.88(1.91)		1633.90	9.28(9.10)	39.19(39.00)

The D and P were calculated based on ρ_0.

By inspecting the molecular density values in Table 2, it was found that the largest and smallest values are 2.05 and 1.31 g/cm^3, respectively. All of the derivatives have increased density relative to the unsubstituted one. However, we should note that the actual densities of aminonitrocyclopentanes may be higher, because the NH$_2$ and NO$_2$ groups of neighboring molecules may attract each other electrostatically and draw the molecular units more tightly together in the condensed phase. As clearly shown in Table 2, the detonation velocity and pressure generally increase as the number of nitro and amine groups increases. However, it is regretful that only derivatives D and E have good detonation performance, and only the detonation properties of E exceed those of HMX, which is one of the most widely used energetic ingredients in various high-performance explosives and propellant formulations. In theory, of all the title compounds, E ($\rho = 2.05$ g/m^3, $D = 9.11$ m/s, $P = 39.62$ PGa) essentially satisfies the quantitative criteria of the energy and stability of an HEDM ($\rho = 1.9$ g/m^3, $D = 9.0$ m/s, $P = 40.0$ PGa). We must be aware however that detonation performance may be overrated if the gas-phase heats of formation are used instead of solid-phase values, shown in the solid-phase heats of formation of highly energetic compounds previously calculated [27, 28].

Bond dissociation energies (BDE)

Generally speaking, compounds with higher energies are less stable. However, the thermal stability of an energetic material determines its applicability. Therefore stability requirements must be considered in the 'molecular design' of HEDMs in addition to their highly energetic properties. Previous studies have shown that the value of the BDE can be used to evaluate the sensitivity and stability of energetic materials.

The bond order is a measure of the overall bond strength between two atoms. Generally, a lower bond order indicates a less stable molecule. Thus, the trigger bond is calculated depending on 'the principle of the smallest bond order' (PSBO). In addition, for nitrocompounds, in general the $C–NO_2$ bond is the weakest one in the energetic molecule and its cleavage is the common initial fission step for energetic materials under heat, impact, and electric spark stimulation [29]. Table 3 lists the bond orders for the $C–NO_2$ bonds and their bond dissociation energies, both without (BDE) and with BDE_{ZPE} correction. The bond order values were obtained by Natural Bond Orbital analysis (NBO) at the same level.

Table 3.   Calculated bond dissociation energies (kJ/mol) and bond orders of $C-NO_2$ bonds at the UB3LYP/6-311G** level

Compound	Bond order	BDE	BDE_{ZPE}
A	0.7524	226.29	205.43
B1	0.7853	173.55	153.57
B2	0.7445	212.56	193.33
C1	0.7551	124.00	99.23
C2	0.7414	168.64	149.50
D	0.7510	114.50	96.54
E	0.7295	64.67	46.23

It was found that the BDE value shifts to a lower value by ca.17-24 kJ/mol when the ZPE correction is included. It is obvious that the pyrolysis mechanism is not affected by the ZPE correction. Actually, the same conclusion has been reached for other systems [30]. Inspecting the values in Table 3, it was found that the BDE values decrease as the number of substituent groups increase. The position of the substituent groups has an important effect on the BDE. Generally speaking, the closer the substituent groups are to one another, the smaller is the BDE. For example, the distance between the substituent groups in C1 is less than that in C2, so the BDE of C1 is smaller than that of C2. All of the derivatives have high BDEs except for E. We suggest two reasons to explain why, of all the

derivatives, E has the smallest BDE value. Firstly, the influence of hydrogen bonding may be disregardful in homolysis reactions; secondly, steric hindrance between substituents reduces the stability of E.

Impact sensitivity

The prediction of the impact sensitivity of HEDMs is a very important step for the development of new highly energetic materials. Impact sensitivity is usually characterized by a drop hammer test. It is defined by the height H_{50} from which a given weight falling upon the compound has a 50% probability of producing an explosion. Many studies [31-33] have been carried out at the molecular level to estimate impact sensitivity. In this paper, H_{50} was calculated by two different methods. $^aH_{50}$ was calculated by Eq. (14), in which the Q_{NO2} was calculated by formula (16):

$$Q_{NO2} = Q_N + Q_{O1} + Q_{O2} \qquad (16)$$

where Q_N, Q_{O1} and Q_{O2} are the net charges on the N and O atoms in the nitro group, respectively. In this case, the Q_{NO2} with the smallest absolute Mulliken net charge value was employed.

The OB_{100} was obtained via Eq. (17):

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO})/ M \qquad (17)$$

where: n_O, n_H, and n_C represent the numbers of O, H, and C atoms, respectively; n_{COO} is the number of COO groups, and here $n_{COO} = 0$ for the aminonitrocyclopentanes; M is the molecular weight.

$^bH_{50}$ was calculated according to Eq. (15).

Table 4 lists the Q_{NO2}, OB_{100}, $^aH_{50}$, σ_+^2, v, and $^bH_{50}$ values. For comparison, the relevant values for HMX also are listed in this table. An apparent trend is that the $^aH_{50}$ values decrease as the number of substituent groups increase, which indicates that the sensitivity increases from A to E. Moreover, it is observed from the nitro charge and the $^aH_{50}$ values, that a larger absolute nitro charge value correlates with a higher $^aH_{50}$ value. Compared with the $^aH_{50}$ of HMX, our designed derivatives A, B1, B2, C1, C2, and D have lower sensitivities, and A has the lowest sensitivity of all derivatives. Inspecting the $^bH_{50}$ values in Table 4, we obtained an analogous conclusion to $^aH_{50}$. According to $^bH_{50}$, all derivatives have a lower sensitivity than HMX. However, we also note that the conclusions from $^aH_{50}$ and $^bH_{50}$ are not very consistent with the results from the BDE. For example, the BDE of C1 is smaller than that of C2, but this is not the case from

the point of view of $^aH_{50}$ and $^bH_{50}$. This supports the viewpoint of Politzer [34] that any correlation between bond strength and impact sensitivity is not general, but limited within certain classes of molecules.

Table 4. Calculated characteristic heights (H_{50}, cm) at the B3LYP/6-311G** level

Compound	Q_{NO2}	OB_{100}	$^aH_{50}$	σ_+^2	ν	$^bH_{50}$
A	-0.309	-7.69	100.30	39.3396	0.2216	49.83
B1	-0.228	-5.26	55.00	97.7349	0.2407	54.06
B2	-0.287	-5.26	84.97	80.7616	0.2463	55.51
C1	-0.230	-4.00	55.47	129.5923	0.2165	48.03
C2	-0.208	-4.00	45.96	122.4064	0.2043	45.11
D	-0.194	-3.23	40.15	164.2676	0.1835	39.83
E	-0.150	-2.70	25.04	178.8565	0.1685	36.15
HMX						32.00

^{a} obtained according to Eq. (14)
^{b} obtained according to Eq. (15)

Here it should be noted that Eq. (15) is designed for use with nitramines, so the results for impact sensitivity from Eq. (15) may have significant errors for non-nitramine compounds. Consequently, in order to estimate the sensitivities of these nitro-compounds, the 'available free space per molecule in the unit cell (ΔV, Å^3)' was calculated according to references [35, 36]. The formula: $\Delta V = V_{eff} - V_{int}$, where V_{eff} corresponds to zero free space, V_{eff} = molecular mass/density, V_{int} is the intrinsic gas phase molecular volume, can be appropriately defined as the volume enclosed by the 0.003 a.u. contour of the molecule's electronic density. Calculated ΔV, V_{eff}, and V_{int} values are listed in Table 5.

Table 5. Available free space per molecule in the unit cell (ΔV, Å^3) at the B3LYP/6-311G** level

Compound	V_{int} (0.003)	V_{eff}	ΔV
A	74.59	100.71	26.12
B1	96.27	118.77	22.5
B2	96.94	126.10	29.16
C1	118.26	149.80	31.54
C2	117.45	148.98	31.53
D	139.64	172.10	32.46
E	160.73	200.59	39.86

By inspection of the values in Table 5, it is found that ΔV increases gradually from A to E, which indicates that their impact sensitivities rise as the number of substituent groups is increased. For all of the aminonitrocyclopentanes, we found that the ΔV values vary from 22.50 to 39.86 Å^3, which implies (Ref. 36, Figure 3) that the H_{50} values vary from 200 to 140 cm. The conclusion from the ΔV values is not very consistent with the results from $^aH_{50}$ and $^bH_{50}$. This significant divergence indicates that different methods for calculating impact sensitivities should be used for different classes of HEDMs.

Conclusions

The fully optimized structures of 7 energetic compounds have been obtained at the B3LYP/6-311G** level. The model compounds satisfy the criteria for high energy materials. It was found that introduction of nitro and amine groups reduces the heats of formation and improves the theoretical molecular density. So, based on its high molecular density, E has excellent detonation velocity (9.11 m/s) and pressure (39.62 GPa). The large bond dissociation energies suggest that most of the aminonitrocyclopentanes have good thermodynamic stability. Moreover, most of the compounds have larger H_{50} values than HMX, which represents a lower impact sensitivity.

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