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Theoretical Studies on the Vibrational Spectra, Thermodynamic Properties, Detonation Properties, and Pyrolysis Mechanisms for Polynitroadamantanes

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To look for high energy density materials (HEDM), the relationships between the structures and the performances of polynitroadamantanes (PNAs) were studied. The assigned infrared spectra of PNAs obtained at the density functional theory (DFT) B3LYP/6-31G* level were used to compute the thermodynamic properties on the basis of the principle of statistical thermodynamics. The thermodynamic properties are linearly related with the number of nitro groups as well as with the temperatures. Detonation properties of PNAs were evaluated by using the Kamlet−Jacobs equation based on the calculated densities and heats of formation for titled compounds, and it is found that only when the number of nitro groups of PNA is equal to or more than eight can it be possible for PNAs to be used as HEDMs. The relative stabilities of PNAs were studied by the pyrolysis mechanism using the UHF-PM3 method. The homolysis of the C−NO_2 bond is predicted to be the initial step of thermal decomposition. The activation energies (E_a) for the homolysis decrease with the number of nitro groups being increased on the whole. The stability order of dinitroadamantane isomers derived from the interactions among nitro groups is consistent with what is determined by E_a. The relations between the E_a's and the electronic structure parameters were discussed. In combination with the stability, PNA (1,2,3,4,5,6,7,8,9,10-) is recommended as the target of HEDM with insensitivity.

1. Introduction

High energy density materials (HEDMs) have been receiving heated attention because of superior explosive performances over conventional energetic materials.[1−5] Because of strain energy and compact structures, organic cage compounds are investigated as an important category of HEDMs. Typical examples of these compounds are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC). Recently, another type of organic cage compounds, polynitroadamantanes (PNAs; see Figure 1 for the structure of the parent compound adamantane), which are formed when the H atoms combined to the C atoms are substituted by nitro groups with different number, are also investigated as promising candidates for HEDMs.[2,6] Unlike ONC and CL-20, which possess large strain energy, PNAs possess the lowest strain energy content due to its negative heat of formation of adamantane.[7,8] Accordingly, the instability of PNAs is mainly caused by the introduction of nitro groups.

Theoretically, there are at most 16 nitro groups in a PNA compound. To the best of our knowledge, PNAs with up to 6 nitro groups have been successfully synthesized.[8−18] Conventionally, a material is considered to be an HEDM if its density ρ is larger than 1.9 g·cm^{-3}, detonation velocity D is greater than 9 km·s^{-1}, and detonation pressure P is higher than 40 GPa.[19] Gilbert and his co-worker calculated the density, heat of formation, and detonation pressure for a series of PNAs with the number of nitro groups ranging from 2 to 16. They found that the optimal number of NO_2 groups in PNA is 11.[2] Pivina et al. evaluated the properties of the isomers of hexanitroadamantane.[20] Škare and Sućceska reported the detonation parameters for 1,3,5,7-PNA.[21] Essentially, the above methods used to calculate explosive properties are of empirical group additivity. An inherent limitation of these methods is that they cannot differentiate isomers that are present in PNAs very frequently.

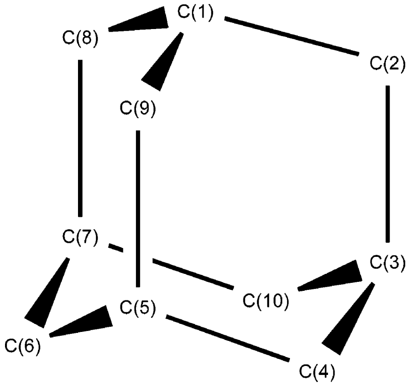

Figure 1. The structure and atomic numbering of adamantane.

Rapid development of computer technology and theoretical chemistry provide us with a more rigid and accurate approach to explosive phenomena. In the present paper, we calculated the detonation velocities and pressures for a series PNAs, using the Kamlet−Jacob equation.[22] Densities and heats of formation necessary for computing detonation parameters are all derived from the density functional theory B3LYP level. The pyrolysis mechanism and thermal stability are investigated by calculating reaction barriers of C−C and C−N bond breaking. Effects of the number of nitro groups and the nitro positions on the detonation performance and thermal stability are investigated.

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We found that, when the number of NO_2 groups, n, is equal to or more than 8, the corresponding PNAs meet the criteria of an HEDM. With the thermal stability taken into account, three PNAs are finally screened out as candidates for potential HEDMs of the PNA series. This finding enables us to search for new high-energy and insensitive explosives among polynitroadmantanes.

This paper is arranged as follows. First, we describe our computational methodology. Results and discussions are presented in section 3, including infrared spectra and thermodynamic properties (subsection 3.1), detonation parameters (subsection 3.2), and thermal stability (subsection 3.3). Following subsection 3.3, the concluding remarks are given.

2. Computational Details

Many studies[23−25] have shown that the DFT B3LYP method[26,27] in combination with the 6-31G*[28] basis set is able to give accurate energies, molecular structures, and infrared vibrational frequencies. In this paper, the geometry optimizations and vibration analyses for PNAs were carried out at the B3LYP/6-31G* level with the *Gaussian 98* program package.[29] Because DFT harmonic vibrational frequencies are usually larger than those observed experimentally, the scaled factor of 0.96 was used as before.[30] The thermodynamic properties of PNAs in the 273−800 K range were derived from the statistical thermodynamic principle.[31]

The detonation velocity and pressure were estimated by the Kamlet−Jacobs equations as in the following expressions

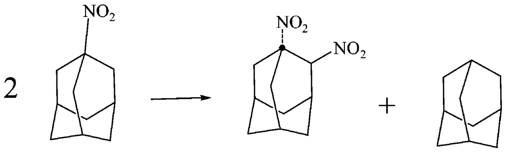
$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \qquad (1)$$

$$P = 1.558{\rho_0}^2NM^{1/2}Q^{1/2} \qquad (2)$$

where each term in eqs 1 and 2 is defined as follows: D, detonation velocity (km/s); P, detonation pressure (GPa); N, moles of detonation gases per gram of explosive; M, average molecular weight of these gases; Q, chemical energy of detonation (kJ·mol^{-1});[25] and ρ_0, density of explosive (g·cm^{-3}). Here, the heats of formation (HOFs) of PNAs were derived by an isodesmic reaction that has been employed very successfully to calculate HOF from total energies obtained from DFT calculations,[23,32−33] and the molecular densities of PNAs were obtained by dividing the average molecular volume by the molecular weight. The average molecular volume of each molecule was yielded from the statistical average value of 100 molar volumes of each molecule. The molar volume of each molecule was calculated by the Monte Carlo method in the *Gaussian 98* program package, which is defined as the volume inside a contour of 0.001 e/Bohr^3 density.[34]

It is very difficult to perform the pyrolysis calculations on large systems, such as PNAs, at the high level. However, semiempirical molecular orbital (MO) methods,[35−38] such as PM3, AM1, MNDO, and MINDO/3 with the unrestricted Hartree−Fock (UHF) model can give satisfactory results,[39−42] and PM3 calculations are fast and very reliable for organic compounds with elements of periods 1 and 2 (C, H, N, and O). Here, UHF-PM3 incorporated in the Mopac 6.0 program package[43] was applied to calculate the pyrolysis of PNAs. Each transition state (TS) was found and confirmed by both the presence of only one imaginary frequency and the analysis of the internal reaction coordinate (IRC).

Designing isodesmic disproportionation reactions at the B3LYP/6-31G* level can be used to calculate the interactions among nitro groups.[44] The computed disproportionation of x molecules of mononitroadamantane ($C_{10}H_{15}NO_2$) to $C_{10}H_{16-x}(NO_2)_x$ plus ($x - 1$) molecules of adamantane ($C_{10}H_{16}$) is very useful to forecast the relative stability of isomers. For example, the repulsion energies among nitro groups of 1,2-dinitroadamantane can be obtained as eq 3



(3)

The disproportionation is defined as energy $E = \Delta E_0 + \Delta ZPE$, 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 energy (ZPE) of the products and the reactants at 0 K.

3. Results and Discussions

3.1. Infrared Spectra and Thermodynamic Properties. As we all know, the IR spectrum is one basic property of a compound, and also an effective measure to analyze or identify substances. Besides, it has a direct relation with the thermodynamic properties. However, for some reason, there has been little experimental data for the IR spectra and thermodynamic properties for PNAs. Therefore, it is of great significance to calculate the IR and thermodynamic properties of PNAs by a theoretical method. Here, all the IR (see Table 1 in the Supporting Information) of PNAs were obtained at the DFT B3LYP/6-31G* level. From the IR spectra of PNAs, it can be seen that there are five main characteristic regions for PNAs compounds. At more than the 2907.6 cm^{-1} range, the modes are associated with the C−H symmetry and asymmetry stretch. At the 1447.4−1499.0 cm^{-1} range, the weaker modes correspond to the C−H scissor stretch. It is remarkable that there are two very strong IR active modes. One is in the 1581.9−1634.1 cm^{-1} range that corresponds to the C−N stretch and the N═O asymmetry stretching motion in nitro groups, and in this region, the number of frequencies equals that of nitro groups, e.g., 1,3,5,7-tetranitroadamantane has four frequencies of 1596.0, 1598.6, 1598.6, and 1601.0 cm^{-1}. The other is associated with the C−N stretch owing to N-atom motion and the N═O symmetry stretching in nitro groups. However, the relative positions of nitro groups have an important effect on the frequencies in this region, e.g., as for the PNAs with nitro groups occupying geminal positions, 2,2-, 1,4,4-, 2,2,4,4-, 1,3,4,4,5,7-, 2,2,4,4,6,6-, and 1,3,4,4,5,7,8-, the corresponding frequencies are in the range 1299.9−1376.1 cm^{-1}, but those of others are in the 1326.2−1382.8 cm^{-1} range. This is attributed to the coupling effect of geminal nitro groups that leads the peaks associated with the N═O stretch to split into two, one moving to a higher frequency and the other to a lower. For example, the frequencies of 1,3-, 1,2-, 1,4-, 2,4-, and 2,6-dinitroadamantanses are at 1375.7, 1382.8, 1381.7, 1377.2, and 1381.0 cm^{-1}, respectively, while those of 2,2-dinitroadamantane are at 1313.4 and 1382.5 cm^{-1}, accordingly. As for adamantane, there is no characteristic peak in these two regions, because it has no nitro group. At the same time, it is found that 1,3,5,7-tetranitroadamantane has a quite compact spectrum, which perhaps is because 1,3,5,7-tetranitroadamantane has such high symmetry (S_4) that its many frequencies overlap and intensities strengthen. For example, there are two frequencies of 1366.4 cm^{-1} with intensity 179.0 km·mol^{-1}. The fifth is the fingerprint

TABLE 1: Partial Experimental and Calculated Frequencies of 1,3,5,7-Tetranitroadamantane[a]

329(m) [305.4]	713(m) [705]	741(m) [722]
1362(s) [1366]	1457(m) [1464]	1542(s) [1599]
748(m) [732.2]	845(w) [815]	1236(m) [1214]
2985(w) [2973]	3000(w) [2974]	3015(w) [3033]

[a] Calculated values are in square brackets. Intensities are in brackets; s, m, and w are present of strong, medium, and weak, respectively.

region, which can be used to identify isomers, and the weak peaks of this region are mainly caused by the torsion of nitro groups.

To testify to the reliability of the theoretical computation, we compared the partial calculated frequencies with the experimental values of 1,3,5,7-tetranitroadamantane[14,15] in Table 1.

As is evident in Table 1, the calculated frequencies of 1,3,5,7-tetranitroadamantane are close to the experimental values available, e.g., the calculated values of 1366, 1464, and 1599 cm^{-1} are well in accord with the experimental values 1362(s), 1457(m), and 1542(s) cm^{-1}. The trivial discrepancy is mainly due to intermolecular interactions in the experiment. Besides, the experimental values of 1- (1366.1, 1533.7 cm^{-1}) and 1,3- (1368.0, 1545.6 cm^{-1})[9] are also quite consistent with the calculated values (1377.4, 1581.9 cm^{-1}) and (1375.7, 1589.2 cm^{-1}). All of these prove the reliability of the computational IR.

According to the calculated IR, thermodynamic properties of them ranging from 273 to 800 K were also obtained on the basis of the principle of statistic thermodynamics. (See Table 2 in the Supporting Information). From these data, it was found that all the thermodynamic functions increase with increasing temperature. With 1,3,5,7-tetranitroadamantane as an example, the temperature-dependent functions for $C^{\circ}_{\mathrm{p,m}}$, S°_{m}, and H°_{T} (thermal correction) in the range 273.15−800 K can be expressed as the following

$$C^{\circ}_{\mathrm{p,m}} = -19.7527 + 1.2839T - 0.0006T^2$$

$$S^{\circ}_{\mathrm{m}} = 252.4003 + 1.2060T - 0.0003T^2$$

$$H^{\circ}_{\mathrm{T}} = 87.9109 - 0.2966T + 0.0007T^2$$

and the correlation coefficients R^2 are 0.9999 and 1.0000, and 0.9805, respectively. Meanwhile, $\mathrm{d}C^{\circ}_{\mathrm{p,m}}/\mathrm{d}T = 1.2839 - 0.0012T$, $\mathrm{d}S^{\circ}_{\mathrm{m}}/\mathrm{d}T = 1.2060 - 0.0006T$, and $\mathrm{d}H^{\circ}_{\mathrm{T}}/\mathrm{d}T = -0.2966 + 0.0014T$. It is obvious that the gradients of $C^{\circ}_{\mathrm{p,m}}$ and S°_{m} to the temperature decrease, but that of H°_{T} increases as temperature increases.

In addition, all the thermodynamic functions increase as the number of nitro groups (n) increases. The following equations show the relations between n and $C^{\circ}_{\mathrm{p,m}}$ and S°_{m} at 298.15 K, and the correlation coefficients are all more than 0.99.

$$C^{\circ}_{\mathrm{p,m}} = 151.7517 + 38.4599n$$

$$S^{\circ}_{\mathrm{m}} = 357.3342 + 52.8113n$$

$$H^{\circ}_{\mathrm{T}} = 21.9183 + 7.0040n$$

One could find that, on average, $C^{\circ}_{\mathrm{p,m}}$, S°_{m}, and H°_{T} increase by 38.5 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, 52.8 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, and 7.0 $\mathrm{kJ \cdot mol^{-1}}$, respectively, when one more nitro group is attached. This shows good group additivity on thermodynamic functions. The above equations and the data in Table 2 of the Supporting Information are helpful for further studies on the other physical, chemical, and explosive properties of PNAs.

TABLE 2: Calculated Total Energy (E_0), Zero-Point Energy (ZPE), Thermal Correction (H_{T}), and Heats of Formation (HOFs) of the PNAs at B3LYP/6-31G* Level

compd[a]	E_0 (au)	ZPE ($\mathrm{kJ \cdot mol^{-1}}$)	H_{T} ($\mathrm{kJ \cdot mol^{-1}}$)	HOF ($\mathrm{kJ \cdot mol^{-1}}$)
2,4,6-	−1004. 2200079	637.24	42.81	−201.62
2,4,6,8-	−1208.7081414	643.34	49.92	−197.53
1,3,4,5,7-	−1413.2024053	644.07	57.51	−214.83
2,4,6,8,10-	−1413.1945473	649.36	56.93	−189.08
1,3,4,5,6,7-	−1617.6785187	649.68	64.53	−179.35
2,4,6,8,9,10-	−1617.6807637	654.78	64.33	−180.34
1,2,3,4,5,6,7-	−1822.147363	655.46	71.29	−133.28
1,2,3,4,5,6,7,8-	−2026.6173365	660.37	77.93	−75.16
2,2,4,4,6,6,8,8,8-	−2026.583114	654.58	78.76	9.73
1,2,3,4,5,6,7,8,9-	−2231.0803474	664.49	84.34	7.79

[a] 2,4,6- Denotes 2,4,6-trinitroadamantane, the others are similar.

TABLE 3: Average Molecular Volumes (V), Densities (ρ), Detonation Velocities (D), and Pressures (P) for PNAs[a]

compd[b]	V	ρ	D	P
1-	135.49	1.34	4.32	6.77
2-	135.50	1.34	4.36	6.92
1,2-	151.45	1.49	5.99	14.12
1,3	151.65	1.49	5.66	12.61
1,4-	152.80	1.48	5.65	12.49
2,4-	147.38	1.53	5.81	13.52
2,6-	151.60	1.49	5.70	12.77
2,2-	150.20	1.50(1.48)[47]	5.79	13. 25
1,3,5-	165.30	1.64	6.49	17.66
2,4,6-	167.41	1.62	6.47	17.41
1,4,4-	165.38	1.64	6.47	17.53
2,4,6,8-	183.57	1.72	7.18	22.72
1,3,5,7-	184.52	1.71	7.11	21.74
2,2,4,4-	180.78	1.75(1.65)[18]	7.35	23.58
2,2,6,6-	178.97	1.77(1.75)[17]	7.32	23.89
1,3,4,5,7-	200.97	1.80	7.75	26.67
2,4,6,8,10-	198.30	1.82	7.84	27.44
1,3,4,5,6,7-	213.55	1.90	8.76	35.15
1,3,4,4,5,7-	210.95	1.92	8.45	32.93
2,4,6 8,9 10-	214.25	1.89	8.33	31.68
1,2,3,4,5,6,7-	231.85	1.95	8.77	35.74
1,3,4,4,5,7,8-	229.64	1.96	8.81	36.21
1,2,3,4,5,6,7,8-	244.66	2.03	9.24	40.59
2,2,4,4,6,6,8,8-	250.23	2.00	9.18	39.82
1,2,3,4,5,6,7,8,9-	267.42	2.02	9.39	41.86

[a] Units: ΔH_{f}, $\mathrm{kJ \cdot mol^{-1}}$; V, $\mathrm{cm^3 \cdot mol^{-1}}$; ρ, $\mathrm{g \cdot cm^{-3}}$; D, $\mathrm{km \cdot s^{-1}}$; P, GPa. [b] 1- and 1,2- denote 1-nitroadamantane and 1,2-dinitroadamantane, respectively; the others are similar.

3.2. Detonation Properties. Detonation velocity (D) and detonation pressure (P) are the important parameters to evaluate the performances of energetic materials. As for C, H, O, and N-containing explosives, they can be estimated using the Kamlet−Jacobs equation.[45,46] Here, besides the compounds taken from ref 33, some others are supplemented as listed in Table 2, and all of their HOFs are obtained by designing an isodesmic reaction as in ref 33. The average molecular volumes (V), densities (ρ), D, and P for PNAs are listed in Table 3.

From Table 3, it is found that the calculated value 1.75 $\mathrm{g \cdot cm^{-3}}$ of 2,2,4,4-tetranitroadamantane is somewhat larger than the experimental value 1.65 $\mathrm{g \cdot cm^{-3}}$, while the theoretical values 1.50 $\mathrm{g \cdot cm^{-3}}$ and 1.77 $\mathrm{g \cdot cm^{-3}}$ of 2,2- and 2,2,6,6- are very close to the corresponding experimental values 1.48 $\mathrm{g \cdot cm^{-3}}$ and 1.75 $\mathrm{g \cdot cm^{-3}}$. All of these further confirm the reliability of the calculated results. As for the isomers, there is no conspicuous discrepancy of their V, ρ, D, and P, respectively. As a whole, V, ρ, D, and P increase with increasing n. For instance, for 2-, 2,4-, 2,4,6-, 2,4,6,8-, 2,4,6,8,10-, and 2,4,6,8,9,10-, their corresponding expressions are as follows:

$$V = 118.13 + 16.08n$$

$$\rho = 1.28 + 0.11n$$

$$D = 4.00 + 0.76n$$

$$P = 2.86 + 4.88n$$

and the coefficients are 0.9986, 0.9875, 0.9830, and 0.9978, accordingly. With respect to 1-, 1,3-, 1,3,5-, 1,3,5,7-, 1,3,4,5,7-, 1,3,4,5,6,7-, 1,2,3,4,5,6,7-, 1,2,3,4,5,6,7,8-, and 1,2,3,4,5,6,7,8,9-, the following expressions are obtained:

$$V = 118.75 + 16.148n$$

$$\rho = 1.34 + 0.086n$$

$$D = 4.40 + 0.621n$$

$$P = 3.71 + 4.56n$$

and the coefficients are 0.9989, 0.9762, 0.9704, and 0.9891, respectively. As for 1,2,3,4,5,6,7,8,9,10- (it is too large, and the vibration analysis of it cannot be done), on the basis of the above expressions, its V, ρ, D, and P values of 280.23 cm^3·mol^{-1}, 2.20 g·cm^{-3}, 10.6 km·s^{-1}, and 49.31 Gpa, respectively. were evaluated. Although the limitations of the calculation method leads these data perhaps to be bigger than the experimental values, these results are still interesting in that the two PNAs (1,2,3,4,5,6,7,8,9- and 1,2,3,4,5,6,7,8,9,10-) have better detonation performances than HMX, and even than hexanitrohexaazaisowurtzitane (CL-20), regarded as the best high energy insensitive explosive containing C, H, N, and O, presently. This shows their potential value as energetic materials. According to the usual criterion that, as an HEDM, properties should be $\rho > 1.9$ g·cm^{-3}, $D > 9$ km·s^{-1}, and $P > 40$ Gpa, only when n is equal to or more than eight will PNAs meet the requirements of HEDM.

3.3. Thermal Stability. As a high energy insensitive explosive, its thermal stability should also be emphasized. To elucidate this, two possible initial steps in the pyrolysis route of PNAs were considered in Table 4: (1) breaking the C−NO$_2$ bond and (2) breaking the C−C bond on the skeleton. It should be pointed out that, in this work, we selected the weakest C−C or C−NO$_2$ bond based on the Mulliken population analyses as the initially breaking bond.

In Table 4, although only 13 PNAs were studied by both of the two possible initial steps in all, it is enough to show that E_a's for breaking C−NO$_2$ bonds are much smaller than those for breaking C−C bonds of PNAs, so the initial step in the pyrolysis is the rupture of the C−NO$_2$ bond, which is consistent with the experimental conclusion.[48] Previous studies have shown that homolysis of the N−NO$_2$ bond is preferential for CL-20 (HNIW),[49] but homolysis of the C−C bond is the initial step in the pyrolysis of polynitrocubanes because of the higher strain energies,[25] so there is no certain rule of the pyrolysis for caged organic compounds, and their pyrolysis mechanisms are mainly decided by the structures, especially the cage skeletons.

TABLE 4: HOFs of the Reactants, Transition States, and Activation Energies (E_A) for the Homolysis of C−C and C−NO$_2$ Bond of PNAs Using UHF-PM3 Method[a]

	heat of formation (kJ·mol^{-1})			E_a (kJ·mol^{-1})	
		TS			
cmpd[b]	reactants	C−C	C−NO$_2$	C−C	C−NO$_2$
1-	477.60	663.77	621.66	186.17	144.06
2-	485.00	668.65	630.12	183.65	145.12
1,2-	498.92	661.15	630.01	162.23	131.09
1,3	483.23	674.17	621.27	191.04	138.04
1,4-	487.09	674.11	628.24	187.02	141.15
2,4-	498.44	683.07	638.79	184.63	140.35
2,6-	493.05	677.41	635.48	184.36	142.43
2,2-	535.73	707.09	635.98	171.36	100.25
1,3,5-	499.07	695.03	631.41	195.96	132.34
2,4,6-	515.96		651.23		135.27
1,4,4-	545.08	719.10	641.72	174.02	96.64
1,2,3-	533.28	694.21	650.30	160.93	117.02
1,3,8-	510.85		636.63		125.78
1,3,6-	500.88		635.56		134.68
1,3,5,7-	523.96	729.43	651.24	205.47	127.28
2,4,6,8-	555.99		682.18		126.19
2,2,4,4-	649.74	826.75	731.40	177.01	81.66
1,4,4,7-	564.62		659.76		95.14
2,2,6,6-	606.21		703.64		97.43
1,3,4,5,7-	592.61		692.52		99.91
2,4,6,8,10-	598.29		721.31		123.02
2,2,4,4,6,6-	778.29		848.69		70.40
1,3,4,5,6,7-	657.83		750.84		93.01
2,4,6,8,9,10-	642.75		761.76		119.01
1,2,3,4,5,6,7-	743.90		837.25		93.35
1,3,4,4,5,7,8-	745.42		819.33		73.91
2,2,4,4,6,6,8,8-	979.53		1042.72		63.19
1,2,3,4,5,6,7,8-	820.39		913.29		92.90
1,2,3,4,5,6,7,8,9-	932.45		1026.02		93.57.
1,2,3,4,5,6,7,8,9,10-	1046.12		1121.99		75.87
2,2,4,4,6,6,8,8,10,10-	1343.26		1369.28		26.02
1,2,3,4,4,5,6,7,8,9,10-	1198.78		1223. 55		24.77

[a] All heats of formation are corrected by zero-point energies. [b] 1- and 1,2- denote 1-nitroadamantane and 1,2-dinitroadamantane, respectively; the others are similar.

As a whole, with the number (n) of nitro groups increasing, E_a for the homolysis of C−NO$_2$ bonds decreases. As for 1-, 1,3-, 1,3,5-, 1,3,5,7-, and 2-, 2,4-, 2,4,6-, 2,4,6,8-, 2,4,6,8,10-, 2,4,6,8,9,10-polynitroadamantanes, almost one more nitro group leads E_a to decrease by 5.50 kJ·mol^{-1} or so, but one more geminal nitro group leads E_a to decrease by 16.69 kJ·mol^{-1}, which shows that there is a good group additivity between n and E_a (See Figure 2a,b,c, respectively), and geminal nitro groups have more effect on E_a. At the same time, from Figure 2c, the gradient of E_a first decreases ($n = 1-4$), and then when $n = 5$, E_a dramatically decreases, which is the result of both the repulsion of geminal nitro groups and the superconjugate effects between bond N═O bond and the C−N bond judged by the natural bond orbital analyses.[50] When the number of geminal nitro groups (n) is less than four, both of them act evenly, but when n gets to 5, the repulsion energy dominates, so that the stability descends greatly. In Figure 2d, the first four points are denoted as 1-, 1,3-, 1,3,5-, and 1,3,5,7- ; other points are PNAs (1,3,4,5,7-, 1,3,4,5,6,7-, 1,2,3,4,5,6,7-, 1,2,3,4,5,6,7,8-, and so on) with more ($n = 5-10$) nitro groups; these compounds are rather stable. When $n = 6-9$, E_a varies a little; when $n = 10$, E_a decreases greatly, but the compound is still comparably stable with E_a of 75.87 kJ·mol^{-1}. However, when one more nitro group is added, such as 1,2,3,4,4,5,6,7,8,9,10-, E_a steeply decreases to 24.77 kJ·mol^{-1}, and the compound becomes very unstable. From the above studies, a conclusion could be drawn that, although when n is equal to or more than eight it is possible to find HEDMs of PNAs, because of the instability of PNAs with geminal nitro groups, there are only three PNAs, 1,2,3,4,5,6,7,8-, 1,2,3,4,5,6,7,8,9-, and 1,2,3,4,5,6,7,8,9,10-, that can be used as high energy insensitive materials, and the third one (1,2,3,4,5,6,7,8,9,10-) is the best choice.

The relative positions of nitro groups of PNAs also have an important effect on E_a. As usual, as to isomers, the shorter distance between the nitro groups of the compound, the more

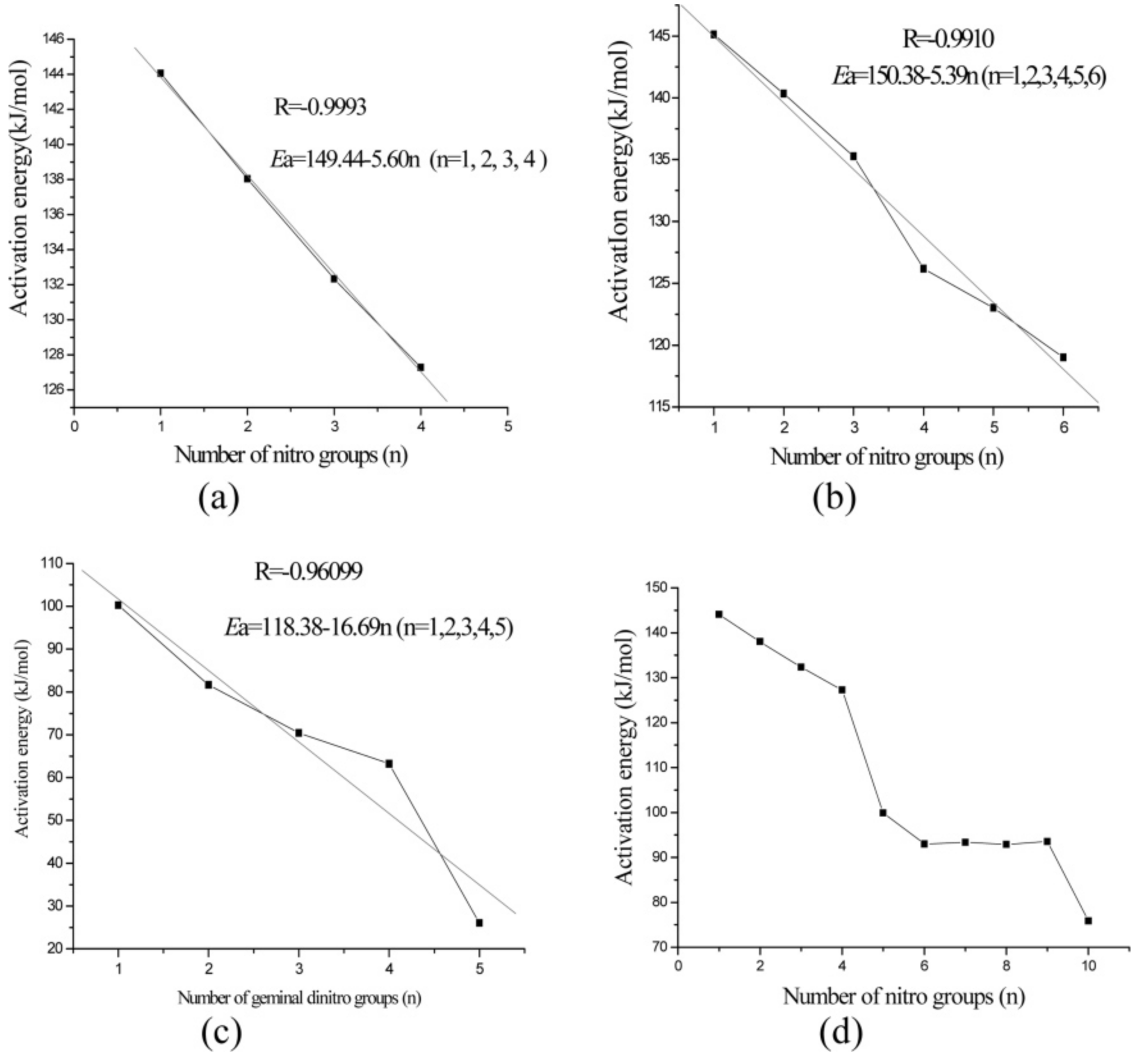


Figure 2. The relationships between E_a and the number of (geminal) nitro groups (n) of (a) 1-, 1,3-, 1,3,5-, and 1,3,5,7-; (b) 2-, 2,4 -, 2,4,6-, 2,4,6,8-, 2,4,6,8,10-, and 2,4,6,8,9,10-; (c) 2,2-, 2,2,4,4-, 2,2,4,4,6,6-, 2,2,4,4,6,6,8,8-, and 2,2,4,4,6,6,8,8,10,10-; (d) 1-, 1,3-, 1,3,5-, 1,3,5,7-, 1,3,4,5,7-, 1,3,4,5,6,7-, 1,2,3,4,5,6,7-, 1,2,3,4,5,6,7,8-, 1,2,3,4,5,6,7,8,9-, and 1,2,3,4,5,6,7,8,9,10-.

unstable the compound will be. The descending order of the distances between the two nitro groups of dinitroadamantane isomers is 2,6 → 1,4 → 2,4- ≈ 1,3 → 1,2 → 2,2-. The two nitro groups of 2,6-, not belonging to the same ring, are the farthest from each other, so this isomer has the biggest E_a and is the most stable of the six isomers. However, 2,2-dinitroadamantane has the smallest E_a and is the least stable. Therefore, the PNAs with geminal nitro have the lowest E_a of all the isomers. At the same time, the E_a's of 1,3- and 2,4-, 1,3,5- and 2,4,6-, 1,3,5,7- and 2,4,6,8- are close to each other, accordingly, which shows that each nitro group, combined to the two different carbons, almost has the same effect on E_a. It is worth noting that the effect of the geminal nitro groups on E_a is even greater than that incurred with the number of $-NO_2$ groups increasing. For instance, the E_a of 2,2-dinitroadamantane is less than that of 1,2,3-, 1,3,8-, and 1,3,6-trinitroadamantanes, and even 1,3,5,7-tetranitroadamantane.

TABLE 5: B3LYP/6-31G* Energies (kJ·mol) for the Disproportionation of x Molecules of Mononitroadamantane ($C_{10}H_{15}NO_2$) to $C_{10}H_{16-x}(NO_2)_x$ Plus ($x - 1$) Molecules of Adamantane ($C_{10}H_{16}$)[a]

cmpd.	E_0 (au)	ZPE ($kJ \cdot mol^{-1}$)	disproportionation energy ($kJ \cdot mol^{-1}$)
1,2-	−799.7245601	629.29	14.00
1,3-	−799.7313861	628.60	11.36
1,4-	−799.7286600	629.58	7.53
2,2-	−799.7112297	628.29	40.03
2,4-	−799.7233471	630.65	10.58
2,6-	−799.7259619	630.89	3.96
1,3,5-	−1004.2111446	634.20	32.41 (34.08)
2,4,6-	−1004.2200079	637.24	21.57 (25.12)
1,3,5,7-	−1208.7215379	639.27	63.07 (68.16)
2,4,6,8-	−1208.7081414	643.34	54.45 (50.23)
2,4,6,8,10-	−1413.1945473	649.36	91.78 (92.78)
2,4,6,8,9,10-	−1617.6807637	654.78	129.02 (138.83)

[a] Values in parentheses are the disproportionation energies that would be obtained if the reaction energies in the dinitroadamantanes were additive.

The data in Table 4 also showed that the six dinitroadamantane isomers have different E_a's. By analysis, it is attributed to the disproportionation repulsion energy. The six disproportionation energies (in Table 3) of 1,2-, 1,3-, 1,4-, 2,2-, 2,4-, and 2,6-dinitroadamantanes were calculated at the B3LYP/6-31G* level. As we expected, the greater the repulsion energy is the less stable the compound will be. The stability order derived from the disproportionation energy in Table 5 is completely consistent with that deduced by the pyrolysis mechanism. Of them, 2,2- has the largest disproportionation energy, and the descending order of the energies is 2,2 → 1,2 → 1,3- ≈ 2,4 → 1,4 → 2,6-. The repulsion energy of another PNA with more

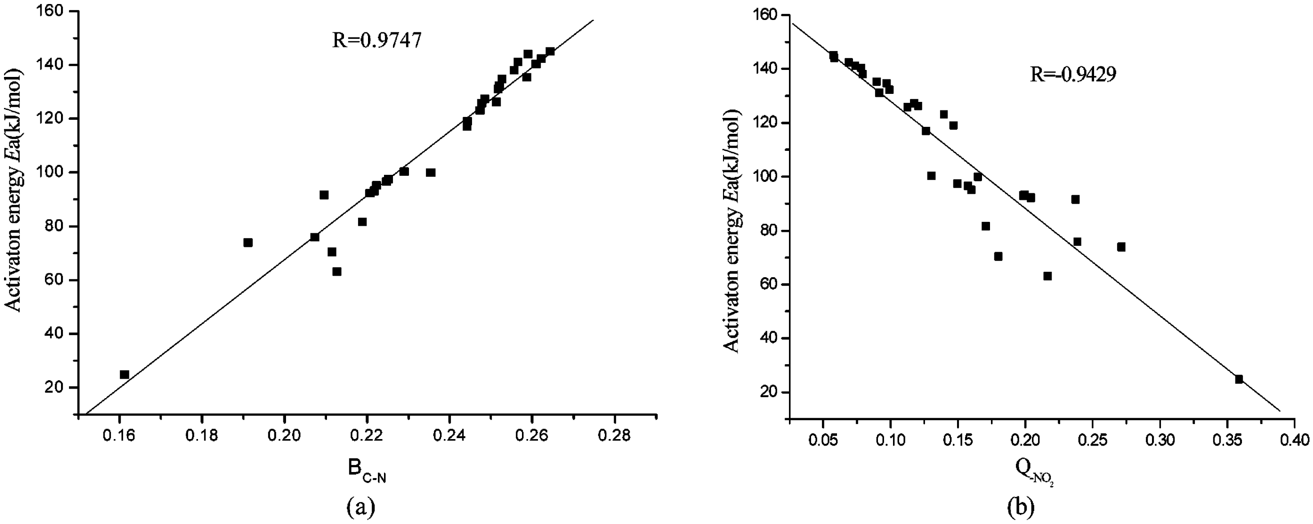


Figure 3. The relationship between E_a and (a) C−N bond orders (B_{C-N}) and (b) net charges on nitro group (Q_{NO_2}).

nitro groups is the total effect of many kinds of disproportionation energies, not equal to direct summation of the six kinds of disproportionation of dinitroadamantane. For example, 1,3,5- and 1,3,5,7- have three and six 1,3 disproportionation energies, separately, but their calculated repulsion energies of 32.41 and 63.07 kJ·mol^{-1} are not equal to the value in parentheses that would be obtained if the disproportionation energies in the dinitroadamantanes were additive. The same phenomenon exists in 2,4,6,8-, 2,4,6,8,10-, 2,4,6,8,9,10-, and so on. However, the average repulsion energies increase with increasing number of nitro groups *n*, and the stabilities decrease correspondingly on the whole, which is also in accord with the conclusion drawn from the relationship between E_a and *n*.

In addition, E_a is also related to the electronic structure parameters, such as bond orders of C−N (B_{C-N}) and the net charge distribution on the nitro group (Q_{NO_2}). From Figure 3, the linear relationships between E_a and B_{C-N}, as well as with ΔE of these thirty-one compounds, are good, and the coefficients are 0.9747 and 0.9429, respectively. Previous static and dynamic MO studies have suggested that "the principle of the smallest bond orders" (PSBO)[39−42,51−54] can be used to identify the thermal stability and impact sensitivity for energetic materials of the same species. Here, the good linear relation between E_a and B_{C-N} proves the reliability of the principle again.

4. Conclusions

From the above calculations, the conclusions of this work are as follows:

(1) The IR spectra of polynitroadamantanes have five characteristic regions. They are assigned to the asymmetry and symmetry stretches of C−H, the C−N stretch owing to N-atom motion and the N=O asymmetry stretching motion in nitro groups, the scissor stretch of the C−H bond, the C−N stretch owing to N-atom motion and the N=O symmetry stretching motion in nitro groups, and the fingerprint regions.

(2) Thermodynamic properties increase quantitatively with the increasing temperature and number of nitro groups (*n*), and the properties of isomers at the same temperature are close to each other.

(3) The detonation properties of PNAs are improved with increasing *n*. Only when the number of $-NO_2$ groups is equal to or more than eight can PNAs be used as HEDMs.

(4) The initial step in the pyrolysis of polynitroadamantanes is the homolysis of the $C-NO_2$ bond. As a whole, with *n* increasing, the activation energies for breaking the $C-NO_2$ bond decrease. The PNAs with geminal nitro groups are the easiest to pyrolyze and even easier than PNAs with more nitro groups. Considering the stability, there are three PNAs, 1,2,3,4,5,6,7,8-, 1,2,3,4,5,6,7,8,9-, and 1,2,3,4,5,6,7,8,9,10-, that can be used as high energy insensitive materials, and 1,2,3,4,5,6,78,9,10- is the best choice.

(5) The stability order of dinitroadamantane isomers derived from the interactions among nitro groups is consistent with what is determined by E_a.

(6) The activation energies of homolysis of the $C-NO_2$ bond are linearly correlated to the bond orders of the $C-NO_2$ bond and charges on $-NO_2$. The reliability of PSBO for identifying the relative magnitude of impact sensitivity was proven again.

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Supporting Information Available: Two tables of supporting data. This material is available free of charge via the Internet at http://pubs.acs.org.

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