

ARTICLE

Theoretical Studies on Structures and Relative Stability for Polynitrohexaazaadamantanes

Xiao-juan Xu^{a,b}, He-ming Xiao^{a*}, Gui-xiang Wang^a, Xue-hai Ju^a

a. Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China; *b.* Department of Chemistry, Yancheng Normal School, Yancheng 224002, China

(Dated: Received on November 7, 2005; Accepted on February 16, 2006)

The density function theory at the B3LYP/6-31G* level was employed to study the structures, including the total energies (E_{ZPE}), the geometries, the oxygen balances (OB_{100}), the dipole moments, of polynitrohexaazaadamantanes (PNHAAs) and the potential candidates of high energy density compounds (HEDCs). The structural parameters of PNHAAs, such as the the maximum N-NO₂ bond length (LB_{max}), the least N-N Mulliken population (B_{N-N}), the least negative charge on the nitro group (Q_{NO_2}) and OB_{100} , were studied to predict their relative stability or sensitivity (the easiness for initiating a detonation, high sensitivity means low stability). It was found that the same conclusion was drawn from the four parameters. With the number of nitro groups increasing, the stabilities of these compounds decrease. OB_{100} failed in identifying the isomers, but the E_{ZPE} energy and the dipole moment were considered to give more reliable results for the isomers.

Key words: Polynitrohexaazaadamantane, Density functional theory, Sensitivity, Oxygen balance, Mulliken population

I. INTRODUCTION

More and more attention has been paid to high energy density compounds (HEDCs) because of their superior explosive performances over conventional energetic compounds [1-5]. Due to strain energy and compact structures, organic cage compounds have been investigated as an important category of HEDCs. Recently, two series of adamantane and hexaazaadamantane (HAA, which is formed when the six secondary C atoms on the adamantane skeleton are all replaced with N atoms, shown in Fig.1, where all H atoms are omitted) have attracted much attention due to their potential as explosives, propellants or powers [6,7]. We continuously presented reports on the structures and performances for the nitro derivatives of adamantane (PNAs) and derivatives of HAA with -CN, -NC, -ONO₂ groups to find HEDCs [8-11].

Our previous study has shown that HAA had positive heat of formation, while adamantane has negative heat of formation [11]. This result predicted that the nitro derivatives of HAA (PNHAAs) would have better energetic performance than PNAs. PNHAAs belong to the series of nitramine, which have been proved to own better explosive performance as energetic compounds, such as the well-known explosives cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX) and hexanitrohexaazaisowurtzitane (CL-20). Thus, it is of much signifi-

cance to study the structures and performances of PNHAAs to find the candidates of HEDCs.

Up to now, there have been only a few reports on PNHAAs. However, 2,4,6,8,9,10-hexanitrohexaazaadamantane (HNHAA) has attracted researchers' attention to some extent, and its crystal density and heat of formation have been evaluated using experimental or theoretical methods [12,13]. It has been predicted to be a promising HEDC. These progresses are very encouraging and promotes us to investigate them systematically.

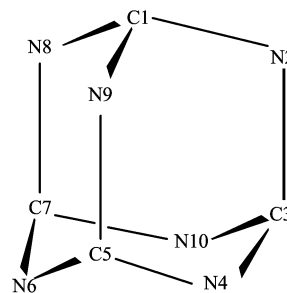


FIG. 1 The structure and atomic numbering of HAA.

Considering the dangers and inconvenience of experiments on energetic compounds, theoretical treatments of energetic molecules receive a wide range of recognition since it provides the necessary data for predicting the structure, spectroscopy, thermodynamic property and so on [14-24]. In this work, we studied the structural and energetic parameters for PNHAAs using the DFT-B3LYP/6-31G* method to predict their relative stability. Such information will be helpful for further investigation as well as molecular design of energetic

*Author to whom correspondence should be addressed. E-mail: xiao@mail.njtu.edu.cn

TABLE I Energies calculated at the B3LYP/6-31G* level for the title compounds

Comp.	E_{ZPE} / (kJ/mol)	E_{HOMO} / a.u.	E_{LUMO} / a.u.	ΔE / a.u.
2-	-1814137.04	-0.24062	-0.05279	0.18783
2,4-	-2351654.48	-0.25980	-0.06829	0.19151
2,6-	-2351681.73	-0.27282	-0.06885	0.20397
2,4,6-	-2888515.75	-0.29001	-0.08626	0.20375
2,4,9-	-2888511.76	-0.28686	-0.08701	0.19985
2,4,10-	-2888500.54	-0.27617	-0.08271	0.19346
2,4,6,8-	-3425356.08	-0.30730	-0.10071	0.20659
2,4,6,9-	-3425342.18	-0.30658	-0.09947	0.20711
2,4,6,8,10	-3962183.86	-0.32079	-0.11208	0.20871
2,4,6,8,9,10-	-4499000.54	-0.33901	-0.12217	0.21684

compounds.

II. COMPUTATIONAL METHOD

The title molecules obtained with Chem3D software were fully optimized at the B3LYP/6-31G* level [25,26] by the Berny method [27,28]. Population analyses and frequency calculations were performed for each optimized structure. All calculations were performed with the Gaussian 98 program package [29] on a Pentium-IV personal computer in our laboratory. The default convergence cutoffs given in the program were used throughout the computations.

III. RESULTS AND DISCUSSION

A. Energies

Table I gives the total energies corrected by zero point energy (E_{ZPE}), the energies of the highest occupied molecular orbitals (E_{HOMO}), the lowest unoccupied molecular orbitals (E_{LUMO}) and their gap (ΔE) obtained at the B3LYP/6-31G* level.

From Table I, it can be seen that the E_{ZPE} of the title compounds are determined by both the number (n) and the relative position of nitro groups. For isomers with the same n , their energy differences are due to the different repulsions of nitro groups. The shorter the distance between the nitro groups is, the greater the repulsion is, and thus the isomer will own more energy. The isomer with lower energy is more stable than that with higher energy. For example, 2,6- is predicted to be more stable than 2,4-, and the ordering of stability is predicted as 2,4,6- > 2,4,9- > 2,4,10- for these three isomers (2- and 2,4- denote 2-nitrohexaazaadamantane and 2,4-dinitrohexaazaadamantane, respectively, others are similar).

Based on the energies of the HOMO and the LUMO in Table I, we found that when n ranges from 1 to 6, the E_{HOMO} decreases from -0.24062 to -0.33901 a.u., and

the E_{LUMO} decreases from -0.05279 to -0.12217 a.u., but ΔE increases from 0.18783 to 0.21684 a.u. This indicates that the electron transition or transfer reactions become difficult in this case, that is to say, with the number of nitro group increasing, the chemical or optical stabilities of these title compounds perhaps will be improved.

B. Structure parameters

The fully optimized geometric parameters for all the title compounds, including bond lengths, bond angles, and dihedral angles, are listed in Table II-IV.

It can be seen from Table II-IV that all the structure parameters are affected by n , the spacial orientations of the nitro groups, as well as the molecular symmetry. In particular, the average N-N bond length increases with n increasing. To a certain extent, the bond strength can be approximately represented by bond length. Therefore, it can be predicted that with n increasing, it is easier to break down the N-N bond, and the sensitivity of the compound will be higher, provided that the N-N bond is the trigger bond when thermolysis. On the contrary, the average bond length of C-N decreases, the cage skeleton of HAA will be stabilized. For other bond lengths, C-H bonds will be slightly shorten or hardly be changed, and the N-H bonds will almost keep intact as n increases. As to isomers, the shorter the distance between the nitro groups is, the longer the N-N bond will be. For instance, the ordering of relative distances between the nitro groups is 2,4,10- < 2,4,9- < 2,4,6-, but the ordering of the longest N-N bond length (LB_{max}) is 2,4,6- \approx 2,4,9- < 2,4,10-, and 2,4,6,8- < 2,4,6,9-, which indicates that the compound 2,4,6- and 2,4,6,8- may be the most stable compound in their isomers, respectively. This is in good agreement with that drawn from E_{ZPE} mentioned above.

The data of bond angles in Table III also show that all the bond angles of C-N-C, C-N-H, N-C-N, and N-C-H are close to 109.5°, indicating that all the C and N atoms on the skeleton are of sp³ hybridization

TABLE II Calculated Bond length (Å) for the title compounds at the B3LYP/6-31G* level

Comp.	C-N	C-H	N-H	N-N	N=O
2-	1.459-1.496	1.087-1.093	1.019-1.020	1.401	1.226-1.232
2,4-	1.457-1.481	1.085-1.092	1.018-1.020	1.404-1.405	1.223-1.226
2,6-	1.456-1.492	1.086-1.087	1.019	1.405-1.406	1.223-1.231
2,4,6-	1.453-1.492	1.083-1.087	1.018-1.019	1.410-1.414	1.222-1.228
2,4,9-	1.452-1.502	1.083-1.091	1.019-1.020	1.412-1.414	1.221-1.228
2,4,10-	1.458-1.494	1.084-1.087	1.019-1.020	1.410-1.423	1.221-1.228
2,4,6,8-	1.452-1.490	1.083-1.085	1.018	1.416-1.418	1.220-1.226
2,4,6,9-	1.454-1.494	1.084-1.086	1.018-1.019	1.417-1.423	1.218-1.223
2,4,6,8,10-	1.450-1.490	1.083-1.084	1.018	1.425-1.436	1.217-1.220
2,4,6,8,9,10-	1.459-1.479	1.083-1.085		1.430-1.440	1.216-1.218

TABLE III Calculated Bond angle (°) for the title compounds at the B3LYP/6-31G* level

Comp.	C-N-C	C-N-H	N-C-N	N-C-H	C-N-N	N-N=O	O=N=O
2-	108.28-109.71	106.87-110.51	105.15-113.80	108.28-110.59	114.01-114.56	116.86-117.29	125.81
2,4-	108.69-111.58	108.19-110.71	104.90-110.60	108.45-112.73	116.73-118.81	116.86-117.28	126.71-126.78
2,6-	109.67-110.27	108.09-110.45	104.99-112.35	108.44-110.55	113.93-114.45	116.24-116.88	126.18-126.18
2,4,6-	110.20-112.03	109.23-110.45	103.13-113.39	108.57-112.65	113.67-119.20	116.67-117.07	126.67-127.28
2,4,9-	109.37-112.39	108.49-110.26	105.87-112.88	108.66-111.82	113.29-119.28	115.84-116.84	126.79-127.35
2,4,10-	109.44-112.12	109.56-110.89	103.99-115.52	107.95-112.12	114.17-118.99	115.878-116.64	127.21-127.33
2,4,6,8-	110.82-112.08	110.40-112.48	103.31-112.95	109.72-112.50	113.79-118.94	115.73-116.56	127.12-127.65
2,4,6,9-	110.58-112.15	109.45-110.39	103.62-112.23	108.67-112.82	116.08-118.79	115.62-116.49	127.53-127.81
2,4,6,8,10-	111.05-112.59	111.92-112.64	103.37-113.07	109.44-112.03	113.845-118.08	115.72-116.32	127.57-128.32
2,4,6,8,9,10-	112.37-112.88		104.06-112.18	110.48-111.90	114.43-117.96	115.59-115.85	128.45-128.58

TABLE IV Calculated Dihedral angle (°) for the title compounds at the B3LYP/6-31G* level

Comp.	C-N-C-N	N-C-N-H	C-N-C-H	H-C-N-H	H-C-N-N	N-C-N-N	C-N-N=O
2-	53.97-65.39	58.72-65.76	175.46-179.11	55.96-48.49	48.38-48.49	70.90-73.10	19.0-36.60
		175.12-179.68				166.55-168.35	146.55-164.15
2,4-	51.38-64.56	58.65-70.06	174.56-178.90	55.23-60.60	32.41-35.79	82.11-88.92	17.97-26.87
		173.50-180.00				154.43-155.54	157.63-166.53
2,6-	53.38-64.46	62.39-68.03	174.52-179.68	52.52-60.60	48.68-49.02	70.40-72.70	18.82-36.84
		174.63-179.22				166.88-169.51	146.82-164.01
2,4,6-	51.45-65.05	62.70-68.46	173.66-179.45	52.10-57.61	32.78-50.37	74.42-89.43	18.51-37.26
		173.25-179.29				152.90-167.64	145.72-164.38
2,4,9-	53.40-63.58	59.51-67.34	175.75-178.90	55.67-59.91	32.82-48.85	74.50-87.26	15.77-35.09
		175.59-179.29				154.58-167.61	147.34-168.10
2,4,10-	51.19-65.68	63.36-70.53	175.28-178.95	54.81-57.84	31.06-45.50	72.73-93.30	15.80-26.81
		173.58-178.55				151.90-166.94	153.80-168.54
2,4,6,8-	51.59-65.68	66.57-73.26	173.92-179.55	50.40-55.34	33.60-49.82	72.17-88.28	17.94-34.31
		172.33-177.12				156.26-158.71	148.35-165.72
2,4,6,9-	51.87-63.52	62.29-68.34	174.87-178.05	53.72-56.35	34.17-38.07	81.751-90.9	16.84-28.67
		174.29-178.78				156.26-158.71	155.25-167.08
2,4,6,8,10-	50.04-65.51	72.11-73.90	174.56-179.55	49.78-50.09	33.79-48.89	74.37-90.45	16.98-31.67
		171.65-172.19				154.40-169.14	150.63-161.6
2,4,6,8,9,10-	51.36-63.95		175.57-178.48		32.96-45.37	76.44-91.25	13.89-28.60
						153.45-167.27	154.68-169.47

TABLE V The least Mulliken population of the bonds for the title compounds

Comp.	C–N	C–H	N–H	N–N	N=O
2-	0.1937	0.3905	0.2948	0.1721	0.3092
2,4-	0.1950	0.3769	0.2970	0.1564	0.3254
2,6-	0.1881	0.3911	0.2998	0.1685	0.3092
2,4,6-	0.1643	0.3751	0.3061	0.1552	0.3099
2,4,9-	0.1937	0.3747	0.3016	0.1505	0.3142
2,4,10-	0.1741	0.3588	0.3007	0.1558	0.3242
2,4,6,8-	0.1882	0.3738	0.3125	0.1531	0.3075
2,4,6,9-	0.1620	0.3568	0.3102	0.1470	0.3208
2,4,6,8,10-	0.1658	0.3572	0.3134	0.1516	0.3122
2,4,6,8,9,10-	0.1736	0.3537		0.1494	0.3231

type. The N–C–N bond angles deviate farther away from 109.5° than the others, which may be the major origin of the strain energy of HAA. The N atoms on $-\text{NO}_2$ are of sp^2 hybridization. But the O=N=O bond angle is larger than 120° due to the repulsion of the two lone pair electrons of the two O atoms, which leads the N–N=O bond angle to be less than 120° . Meanwhile, it is still found that, with n increasing, the N–N=O bond angle will increase a little due to the more repulsion between the nitro groups. Moreover, for the isomers, the interaction effect of nitro groups can also be well established. For example, the average bond angle N–N=O of 2,4,6- is a little less than that of 2,4,9-, due to its less repulsion energy between the nitro groups. With n increasing, the bond angles of C–N–C and C–N–H become large, while the bond angles of N–C–N decrease gradually, the bond angles of C–N=O and O=N=O change a little, and C–N–N bond angles hardly change. All of these suggest that the geometric parameters of these compounds are determined by both n and the spacial orientations of the nitro groups in isomers.

The dihedral angles in Table IV present that, all the C–N–C–H dihedral angles are close to 180° . Dihedral angles of C–N–C–N and N–C–N–H change a little to keep the skeleton stable with different n . While the differences between the dihedral angles of H–C–N–N, N–C–N–N and C–N–N=O are distinct, indicating that each PNHAA perhaps exists in various configuration isomers due to the spacial orientations of the nitro groups. Therefore, each PNHAA can form many types of crystal with different structure and density possibly.

Mulliken population is a concept that reflects the electron density around this bond. Generally, the less Mulliken population the bond has, the less the electron density around the bond is, and the more easily the bond breaks. Table V lists the least Mulliken population of each kind bond for the title compounds.

It can be seen from Table V that the N–N and the C–N bonds have less Mulliken population, and the N–N bonds have the least in each molecule. This predicts that the N–N bond with least Mulliken population

is the trigger bond during the preliminary thermolysis processes. Meanwhile, on the whole, the average least Mulliken population of the N–N bonds ($B_{\text{N-N}}$) decreases with the increasing n in each molecule except 2,4,6,8,10-. According to the principle of smallest bond order (PSBO) [14,30], we thought that the homolysis of the N–N bond becomes easy and the stability of compound decreases. That is to say, the sensitivity of the compounds increases as n increases, which is similar to that drawn from bond length (LB_{max}). But the ordering of relative stability obtained from $B_{\text{N-N}}$ for isomers is not well consistent with that from LB_{max} . Taking the repulsion energy of nitro groups into account, we thought that the LB_{max} parameter could give more creditable result than that of the other parameters for isomers.

Our previous studies [10,14] have shown that, just like PSBO, the charges on the nitro groups (Q_{NO_2}) can also give comparable results of the relative stability or impact sensitivity of the nitro groups with similar structure. Here, we provide the least Mulliken net charges on the nitro groups of each PNHAA in Table VI.

TABLE VI Minimal negative charges on the nitro groups in the title compounds at the B3LYP/6-31G*level

Comp.	Q_{NO_2}	Comp.	Q_{NO_2}
2-	-0.164	2,4,10-	-0.083
2,4-	-0.132	2,4,6,8-	-0.066
2,6-	-0.145	2,4,6,9-	-0.073
2,4,6-	-0.104	2,4,6,8,10-	-0.038
2,4,9-	-0.103	2,4,6,8,9,10-	-0.030

From Table VI, it can be seen that with n increasing, the average charges on the nitro groups decrease on the whole, indicating that the net charges on the groups redistribute, which will decrease the repulsion energies of the nitro group to keep the molecular stability. On the other hand, it is thought that the more negative charges on the nitro group are, the lower the electron-attraction ability is, and the more stable the nitro com-

pound becomes. From this, we could also deduce that the sensitivity of these compounds increases with n increasing, and the relative stability of the isomers with the same n can also be distinguished by Q_{NO_2} , which is completely consistent with that drawn from $LB_{\text{N-N}}$. For instance, the stability ordering of the isomers with three nitro groups is also be thought as 2,4,6- > 2,4,9- > 2,4,10- by Q_{NO_2} .

Correlations between the impact sensitivity and oxygen balances reported by Kamlet and Adolph are probably the most widely applied in the area of energetic materials research [31]. The oxygen balances of these compounds listed in Table VII are calculated from Eq.(1)

$$OB_{100} = \frac{100(2n_o - n_h - 2n_c - 2n_{\text{coo}})}{M} \quad (1)$$

where n_o , n_h and n_c represent the numbers of the atoms of the corresponding elements in the molecule. n_{coo} is the number of carboxyl groups and equals zero here because there are no carboxyl groups in these compounds, and M is the molecular weight.

TABLE VII Oxygen balance for the title compounds

Comp.	OB_{100}	Comp.	OB_{100}
2-	-7.0	2,4,10-	-1.3
2,4-	-3.4	2,4,6,8-	0.6
2,6-	-3.4	2,4,6,9-	0.6
2,4,6-	-1.3	2,4,6,8,10-	1.9
2,4,9-	-1.3	2,4,6,8,9,10-	2.9

It has been suggested by Kamlet that the lower the oxygen balance OB_{100} is, the lower the sensitivity becomes. It is much clear from Table VII that, on the whole, with the increased n , the OB_{100} of these compounds increase. Thus, their relative stability was predicted to decrease, but their sensitivity increase. However, the OB_{100} failed in distinguishing the relative stability of isomers.

The molecular dipole moment reflects the symmetry of molecule structure and the distribution of atomic charge, and determines the stability in different solvents, too. Table VIII lists the dipoles obtained at the B3LYP/6-31G* level for the ten PNHAAs. It is interesting that there are differences in dipole moments for the isomers due to the different symmetries. For the isomers, the higher the symmetry of a compound is, the more stable it is, and the less energy it will have. By this, we can deduce that 2,6- is more stable than 2,4-, and the stability ordering of the three isomers with three nitro groups is 2,4,6- > 2,4,9- > 2,4,10-, and 2,4,6,8- > 2,4,6,9, respectively, such a trend is in good agreement with that obtained from the E_{ZPE} . Thus, we think that the dipole moment and E_{ZPE} will be more suitable for the estimation of the relative stability of isomers. By these data, it could also be predicted that polar solvent would be able to change the ordering of

the relative stability of the isomers, especially for those with larger dipole moments.

TABLE VIII Dipole moments for the title compounds

Comp.	Mol. dipole	Comp.	Mol. dipole
2-	4.2801	2,4,10-	7.3554
2,4-	7.1663	2,4,6,8-	2.7845
2,6-	2.0265	2,4,6,9-	6.0255
2,4,6-	4.3991	2,4,6,8,10-	2.4608
2,4,9-	6.5346	2,4,6,8,9,10-	0.8048

From the above studies, we found that the relative stability of these compounds could be estimated from $B_{\text{N-N}}$, LB_{max} , Q_{NO_2} , and OB_{100} . In the same way, there are many other ways to do this, such as the heat of formation and the intensity of N-N stretching motion. And it was found that with n increasing, the stability of the title compound decreases, but the sensitivity increases. Certainly, although these parameters are able to qualitatively ascertain the relative stability for a series of compounds with similar structures and thermolysis mechanisms, it is more reasonable to judge the stability or sensitivity of the energetic compound quantitatively by dynamic calculations, which will be our succeeding work.

IV. CONCLUSION

According to the DFT calculations on the nitro derivatives of hexaazaadamantane (PNHAAs) at the B3LYP/6-31G* level, we can draw the following conclusions. The energy gap (ΔE) of the front orbitals increases with n increasing, indicating that the electron transition or transfer reactions will become difficult. The structure parameters of the title compounds are determined by both the number (n) and the spacial orientations of the nitro groups. The relative stability of these compounds could be estimated from $B_{\text{N-N}}$, LB_{max} , Q_{NO_2} and OB_{100} . It is found that with n increasing, the stability of the title compound decreases, but the sensitivity increases. The dipole moment and E_{ZPE} are more suitable for the estimation of the relative stability of isomers.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.10576016 and No.10576030).

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