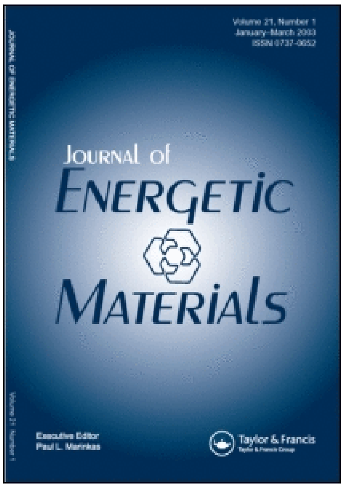

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Theoretical Studies on Pentanitromonoacetylhexaazaisowurtzitane (PNMAIW) by AM1 and PM3 Methods

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We use AM1 and PM3 semiempirical methods to conduct theoretical studies on possible polymorphs of pentanitromonoacetylhexaazaisowurtzitane (PNMAIW), and the close relationship, especially in sensitivity, between PNMAIW and four common nitramine explosives including hexanitrohexaazaisowurtzitane (HNIW) is set up. We forecast that the polymorphs of PNMAIW and HNIW are very alike, and the average real lengths of N—N, C—N and C—C bonds are 0.1403, 0.1455, and 0.1572 nm for A- and C-PNMAIW, 0.1398, 0.1453, and 0.1573 nm for B-PNMAIW, and 0.1396, 0.1452, and 0.1575 nm for D-PNMAIW. The heat of formation of PNMAIW in solid phase is about 152 kJ·mol^{-1}. The impact and shock sensitivities of PNMAIW are predicted to be lower than that of HNIW.

Keywords: Pentanitromonoacetylhexaazaisowurtzitane, modeling, AM1, PM3

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Introduction

Hexanitrohexaazoisowurtzitane (HNIW), also known as CL-20, is the most powerful explosive ever tested [1–3]. HNIW was prepared at our laboratory from tetraacetyldibenzylhexaazaisowurtzitane (TADBIW) or tetraacetylhexaazaisowurtzitane (TAIW) and contains 1.0–1.5% pentanitromonoacetylhexaazaisowurtzitane (PNMAIW), which is believed to be an intermediate when converting TADBIW or TAIW to HNIW [4]. PNMAIW is identified that the acetyl group is on the five-membered rings [5]. PNMAIW has attracted much practical attention. Heretofore there has been no report on a full study of this intermediate because it is difficult to separate from HNIW. Hence, theoretically study of PNMAIW is a good accessible approach.

Computational chemistry has been used to predict the properties of energetic materials and has helped to solve a wide range of chemical problems. Ab initio quantum chemical methods are limited in their practical applicability because of their heavy demands on CPU time and storage space on disk or in the computer memory. Four semiempirical methods were used in the theoretical studies on four different polymorphs of HNIW at our laboratory. Although a considerable distance remains between the experimental and computational results by the AM1 or PM3 method, a combination using the AM1 and PM3 methods is a recommended approach to theoretical study of polycyclic caged nitramine explosives [6]. We suggest that the AM1 method be used for the prediction of lengths and Mulliken populations of N−N, N−C, and N−O bonds, while the PM3 method for lengths of C−C and N−O bonds and heat of formation. N−N bonding Mulliken population by the AM1 method is advised for the forecast of the impact sensitivity of polycyclic caged nitramines. The average differences between the computed and experimental lengths of N−N, N−C, and N−O bonds by the AM1, and C−C and N−O bonds by the PM3, are 0.0011, 0.0029, −0.014, −0.0004, and −0.0012 nm, respectively. Many average differences of other common explosives refer to De Paz and Ciller's work [7] and Xiao's book [8]. PNMAIW is one of the polycyclic caged nitramines. The use of the AM1 and PM3 methods on PNMAIW will be valuable.

In this article our intention is to perform the theoretical studies on possible polymorphs of PNMAIW by the AM1 and PM3 semiempirical methods. Their geometries are fully optimized from the starting geometries based on the polymorphs of HNIW. Vibrational frequency is computed following the previous geometry optimization using the same method at the optimized geometry. We hope that these studies will enable readers to gain a better understanding of this major impurity, and establish a close link between PNMAIW and HNIW, especially in sensitivity.

Computational Methods

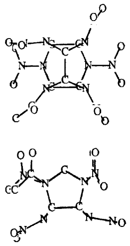
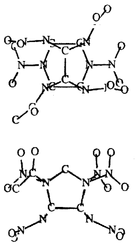
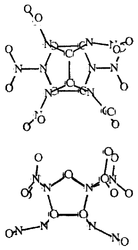
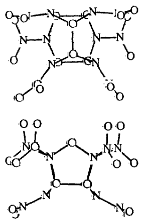
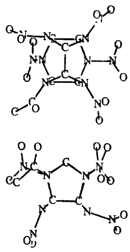
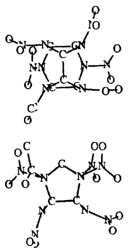
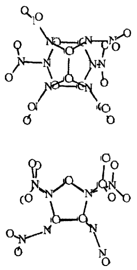
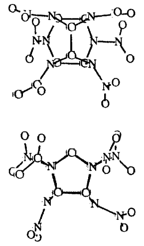
The HyperChem program package [9] was used to create the starting geometries and refine molecular configurations, the Gaussian program package [10] to perform semiempirical molecular orbital computations, and the CS Chem3D Net program package [11] to display all molecular configurations. The molecule was constructed and converted to a 3D structure, with the starting geometry by HyperChem. The starting geometries were based on the polymorphs of HNIW. We used HyperChem to refine the starting geometry, and then Gaussian 98 to perform full geometry optimization and compute vibrational frequency, confirming the optimized geometry by the AM1 and PM3 methods, respectively. For HyperChem, the algorithm used is the Polak-Ribiere algorithm, and the termination condition is the RMS gradient of "0.1 kcal/mol." For Gaussian 98 the algorithm used is the Bemy algorithm, and the cutoff values of maximum force, root-mean-square (RMS) force, maximum displacement, and RMS displacement used to determine convergence are 0.000015, 0.000010, 0.000060, and 0.000040, respectively.

Results and Discussions

Geometries

The PM3 method is better than AM1 to calculate energies of nitro-substituted compounds [7]. According to our study of HINW with four semiempirical methods, we conclude that the PM3 method is also better than the AM1 method to compute energies of polycyclic caged nitramines. So the higher energy conformers of each possible polymorph of PNMAIW by the PM3 method were discarded from the study set. The optimized geometries of four possible polymorphs of PNMAIW by the AM1 and PM3 methods with their hydrogen atoms omitted for clarity are shown in Table 1. A-, B-, C-, and D-forms of PNMAIW correspond to alpha-, beta-, gamma-, and epsilon-polymorphs of HNIW. The spatial orientations of the acetyl and nitro groups of each possible polymorph of PNMAIW are almost the

Table 1
Fully optimized geometries of PNMAIW

	A	B	C	D
AM1				
PM3				

same as those of the corresponding nitro groups of HNIW by the AM1 and PM3 methods. Like the prediction of HNIW, the spatial orientations of the nitro groups with respect to the six-membered ring of each possible polymorph by AM1 are different from those by PM3. So the polymorphs of PNMAIW are predicted to be similar to those of HNIW.

The N−N bond is the most important one in nitramine explosives. The breaking of the N−N bond is considered a key step in thermal decomposition of nitramine explosives. We also select three common nitramine explosives, *N*, *N*-dinitro-1, 2-ethanediamine (DNAE), cyclotrimethylenetrinitramine (RDX), and beta-cyclotetramethylenetetramine (beta-HMX) to compare with the title compound. The longest N−N bond length of each polymorph PNMAIW by the AM1 and PM3 methods is shorter than the corresponding one of HNIW, but nearly longer than those of DNAE, RDX, or beta-HMX except D-PNMAIW. The longest N−N bond length of D-PNMAIW is only 0.0004 nm shorter than that of beta-HMX, and just 0.0002 nm shorter than that of RDX by the AM1 method, indicating that their weakest N−N bond strength is very close. This result also fits those by Milliken population analysis later. The average N−N bond length of each polymorph PNMAIW by the AM1 methods is also shorter than the corresponding one of HNIW, while the average N−N bond lengths by the PM3 method are nearly 0.001 nm shorter than those of HNIW. Hence, PNMAIW is likely more thermodynamically stable than HNIW. The average real N−N lengths of four polymorphs of PNMAIW are estimated to be 0.0011 nm shorter than the corresponding computed ones by AM1. We summarize all of the computed N−N bond lengths (R) and the average ones (Ra) by the AM1 method of four polymorphs of PNMAIW and HNIW along with DNAE, RDX, and beta-HMX in Table 2.

The average differences between the computed and actual lengths of N−C bonds by AM1 and of C−C bonds by PM3 of PNMAIW are predicted to be 0.0029 and −0.0004 nm, respectively. The average lengths of the N−C bond by AM1 and C−C bond by PM3 of PNMAIW and HNIW are listed in Table 3. The average lengths of the OC−C and OC−N bond with respect to the acetyl group of PNMAIW by the AM1 and PM3 methods are also given in Table 3. The average lengths of N−C and C−C of each polymorph of PNMAIW are shorter than or equal to those of HNIW. The OC−N bond length of each polymorph is the shortest among all the C−N bonds. Therefore the OC−N bond could be more stable than the others.

Energies and Thermochemistry Analysis

Thermochemistry analysis was performed at 298.15 K and 101 kPa. The analysis used the standard expressions for an ideal gas in the canonical ensemble. Molecular energies (E_0), the differences (ΔE_{LH}) between the lowest unoccupied molecular orbital energies and the highest occupied molecular orbital energies, zero-point energy corrections (E_{ZPE}), thermal energy corrections (E_T), constant volume molar heat capacities (C_V), and entropy (S) of four polymorphs of PNMAIW and HNIW at the optimized geometries were obtained. According to the definition by semiempirical methods, E_0 is heat of formation in gas

Table 2
Computed N–N bond lengths of PNMAIW and HNIW by the AM1

	R/nm						Ra/nm	$nRa/M/10^{-3}$
A	0.1420	0.1411	0.1398	0.1408	0.1434		0.1414	1.625
alpha	0.1420	0.1400	0.1409	0.1412	0.1420	0.1434	0.1416	1.940
B	0.1421	0.1399	0.1400	0.1408	0.1417		0.1409	1.619
beta	0.1422	0.1401	0.1402	0.1422	0.1418	0.1418	0.1414	1.937
C	0.1419	0.1409	0.1399	0.1433	0.1414		0.1415	1.626
gamma	0.1401	0.1420	0.1412	0.1409	0.1435	0.1420	0.1416	1.940
D	0.1400	0.1413	0.1398	0.1406	0.1416		0.1407	1.617
epsilon	0.1402	0.1401	0.1413	0.1413	0.1418	0.1418	0.1411	1.933
beta-HMX	0.1408	0.1420	0.1393	0.1416			0.1409	1.904
RDX	0.1417	0.1418	0.1418				0.1418	1.916
DNAE	0.1387	0.1388					0.1388	1.851

Table 3
Average computed bond lengths of PNMAIW and HNIW (nm)

	AM1			PM3		
	C–N	OC–C	OC–N	C–C	OC–C	OC–N
A	0.1484	0.1501	0.1416	0.1568	0.1502	0.1458
alpha	0.1486			0.1569		
B	0.1482	0.1502	0.1425	0.1569	0.1502	0.1460
beta	0.1485			0.1569		
C	0.1484	0.1502	0.1419	0.1569	0.1503	0.1457
gamma	0.1486			0.1569		
D	0.1481	0.1501	0.1416	0.1571	0.1502	0.1459
epsilon	0.1483			0.1571		

phase. The PM3 method could predict E_0's to be very close to the experimental value. All of the aforementioned values of PNMAIW and HNIW by the PM3 method are presented in Table 4. The average E_0 of PNMAIW is about 242 kJ·mol^{-1} less than those of HNIW. The real heat of formation of HNIW in solid phase is about 394 kJ·mol^{-1} [3]. De Paz and Ciller have discussed the heats of formation for solid explosives predicted by AM1 and PM3 methods and found that the heats of sublimation are quite similar between members of a given family [7]. According to their results and the similarity of the structures of PNMAIW and HNIW, we reasonably assume the heats of sublimation of PNMAIW and HNIW are nearly the same. Therefore the heat of formation of PNMAIW in solid phase is estimated to be around 152 kJ·mol^{-1}. This magnitude is near to the E_0 values. The order of E_0's is $D > A = C > B$ for PNMAIW, the same to that of HNIW. The values of E_{ZPE}, C_V, and S of the four forms are almost the same and nearly equal to those of HNIW. The magnitudes of E_{LH} and E_T of the four polymorphs are also very close to each other, and around 100 kJ·mol^{-1} greater than those of HNIW. The physical properties of the four polymorphs of PNMAIW are predicted to be similar.

Dipole Moments

The dipole moment in hydrocarbons is due mainly to the atomic charges; only a small fraction is due to lone pairs [12]. It is an important property for energetic materials. Computed dipole moment is a

TABLE 4

Computed energy and thermochemistry results of PNMAIW and HNIW by the PM3

	E_0 (/kJ·mol^{-1})	ΔE_{LH} (/kJ·mol^{-1})	E_{ZPE} (/kJ·mol^{-1})	E_T (/kJ·mol^{-1})	C_V (/J·mol^{-1}·K^{-1})	S (/J·mol^{-1}·K^{-1})
A	212.53	977.60	640.88	710.67	404.60	764.74
B	208.48	957.60	641.17	710.73	404.74	757.76
C	213.57	977.08	640.69	710.52	404.72	766.49
D	216.98	963.14	640.51	710.23	405.37	758.42
alpha	455.00	975.14	546.16	614.86	394.94	762.27
beta	448.70	974.78	546.60	614.96	394.75	755.22
gamma	455.00	975.14	546.16	614.86	394.94	762.27
epsilon	460.36	964.50	545.83	614.49	395.64	757.16

TABLE 5
Computed total dipole moments of PNMAIW and HNIW (Debyes)

	AM1	PM3
A	1.530	1.244
B	1.734	0.8957
C	0.8052	0.9079
D	1.448	1.179
alpha	0.6743	0.2748
beta	0.5690	0.3521
gamma	0.6743	0.2748
epsilon	0.8092	0.2955

measure of the asymmetry in the molecular charge distribution and is given as a vector in three dimensions. The total dipole moments of PNMAIW and HNIW are listed in Table 5. The numerical values of total dipole moments by AM1 and PM3 are greater than those of HNIW. So PNMAIW is predicted to have a stronger dipole moment rather than HNIW, indicating that the centers of positive and negative charge are more relatively apart in molecules than HNIW.

Impact and Shock Sensitivities

The sensitivity of an energetic material to external stimuli is a key property used in determining its potential applications and handling safety. Impact and shock sensitivities are the most commonly used measures for an explosive's tendency to detonate. So we have much concern about the impact and shock sensitivities of PNMAIW.

Nitramines can be induced to decompose by stimuli such as heat, shock, or impact. The thermal decomposition mechanisms are related to its sensitivities. The breaking of the N−N bond is considered a key step in this process and related to impact and shock sensitivities. The smallest N−N bonding Mulliken population is used to forecast impact sensitivity [8].

Our study indicates that the calculated N−N bonding Mulliken population by the AM1 method is verified for the forecast of impact sensitivity of polycyclic caged nitramines [6]. All of the N−N bonding Mulliken populations of PNMAIW, HNIW, DNAE, RDX, and beta-HMX by the AM1 method are shown in Table 6. The smallest N−N

TABLE 6
N–N bonding Mulliken populations by AM1 (a.u.)

	Mulliken population					
A	0.2097	0.2213	0.2142	0.2063	0.2202	
alpha	0.2090	0.2187	0.2148	0.2120	0.2126	0.2057
B	0.2087	0.2206	0.2213	0.2151	0.2177	
beta	0.2076	0.2184	0.2184	0.2076	0.2136	0.2136
C	0.2213	0.2098	0.2151	0.2167	0.2065	
gamma	0.2187	0.2090	0.2120	0.2148	0.2126	0.2057
D	0.2122	0.2221	0.2203	0.2150	0.2217	
epsilon	0.2115	0.2115	0.2194	0.2194	0.2139	0.2139
beta-HMX	0.2229	0.2348	0.2249	0.2160		
RDX	0.2134	0.2134	0.2134			
DNAE	0.2378	0.2378				

bonding Mulliken population of each polymorph of PNMAIW is larger than the corresponding one of HNIW. Those of the D-form are the greatest among all the polymorphs of PNMAIW and HNIW, but less than DNAE, RDX, or beta-HMX. So we estimated the impact sensitivity order of epsilon-HNIW>D-PNMAIW>RDX> beta-HMX>DNAE. The values of the smallest Mulliken population of epsilon-HNIW, D-PNMAIW, RDX, and beta-HMX are nearly equal; hence, the impact sensitivities of the aforementioned four explosives are very close.

The C−N, C−C, OC−N, OC−C, and C−O bonding Mulliken populations of the four forms of PNMAIW by the AM1 method are also obtained. The strength of the OC−N bond with respect to the acetyl group is in the middle of all the C−N bonds. The strength of the OC−C bond with respect to the acetyl group is the most among all the C−C bonds. The strength order of PNMAIW by the AM1 method is C−O>OC−C>C−N>N−N. The N−N bonding Mulliken populations are the smallest among all the bonding Mulliken populations. Table 7 gives the said bonding Mulliken populations of D-PNMAIW by the AM1 method. This tells us that the N−N bond is the weakest one among PNMAIW molecules, and likely to break up first.

A good correlation of nitramine shock sensitivity with all N−N bond lengths and overall molecule size is obtained by (a) explicitly

TABLE 7

Bonding Mulliken populations of D-forms of PNMAIW by AM1 (a.u.)

	Mulliken population					
C–N	0.2792	0.2622	0.2820	0.2507	0.2484	0.2485
	0.2519	0.2625	0.2650	0.2715	0.2661	0.2657
C–C	0.2870	0.3012	0.3062			
OC–N	0.2665					
OC–C	0.3103					
C–O	0.3680					

accounting for each N–N bond and (b) recognizing that the effectiveness of each in initiating decomposition is "diluted" as the molecule becomes larger. These considerations are presented in a straightforward manner as follows [13,14]:

$$\text{Sensitivity} \sim \frac{n\,Ra}{M},$$

where n is the number of N–NO_2 linkages in the molecule, Ra is the average length of all N–NO_2 bonds, and M is the molecule weight, which is taken as a measure of molecule size. This relationship suggests that all N–NO_2 bonds, taken in conjunction with the overall size of the molecule, help to determine the shock sensitivities of nitramines. The N–N bond lengths computed by the AM1 method are used to calculate the values of nRa/M because of the accuracy of the N–N bond lengths of HNIW by the AM1 method. The values of nRa/M of all the aforementioned explosives are summarized in Table 2. All of the values of nRa/M of PNMAIW are nearly equal, and the smallest among those of PNMAIW, HNIW, DNAE, RDX, and beta-HMX. So the shock sensitivities of all forms of PNMAIW are predicted to be almost the same, and the lowest among the said nitramine explosives.

Conclusions

From the above study we give the following predictions and establish the close relationship between PNMAIW and the other four nitramines:

a. By a combination of the AM1 and PM3 semiempirical methods, the optimized geometries of possible polymorphs of PNMAIW are similar to those of HNIW. We forecast that the polymorphs of PNMAIW and HNIW are very alike, and the average lengths of the N−N, C−N, and C−C bonds are 0.1403, 0.1455, and 0.1572 nm for A- and C-PNMAIW, 0.1398, 0.1453, and 0.1573 nm for B-PNMAIW, and 0.1396, 0.1452 and 0.1575 nm for D-PNMAIW.

b. The heat of formation of PNMAIW is about 152 kJ·mol^{-1} in solid phase. The physical properties of the polymorphs of PNMAIW are similar.

c. PNMAIW has a stronger dipole moment than HNIW.

d. The N−N bond is the weakest one among PNMAIW molecule and likely to break up first.

e. Although the impact sensitivities of epsilon-HNIW, D-PNMAIW, RDX, and beta-HMX are very close, that of D-PNMAIW is lower than epsilon-HNIW, and higher than those of DNAE, RDX, and beta-HMX. The shock sensitivity of PNMAIW is the lowest among the nitramine explosives of PNMAIW, HNIW, DNAE, RDX, and beta-HMX.

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