

Crystal density predictions for nitramines based on quantum chemistry

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Abstract

An efficient and convenient method for predicting the crystalline densities of energetic materials was established based on the quantum chemical computations. Density functional theory (DFT) with four different basis sets (6-31G**, 6-311G**, 6-31+G**, and 6-311++G**) and various semiempirical molecular orbital (MO) methods have been employed to predict the molecular volumes and densities of a series of energetic nitramines including acyclic, monocyclic, and polycyclic/cage molecules. The relationships between the calculated values and experimental data were discussed in detail, and linear correlations were suggested and compared at different levels. The calculation shows that if the selected basis set is larger, it will expend more CPU (central processing unit) time, larger molecular volume and smaller density will be obtained. And the densities predicted by the semiempirical MO methods are all systematically larger than the experimental data. In comparison with other methods, B3LYP/6-31G** is most accurate and economical to predict the solid-state densities of energetic nitramines. This may be instructive to the molecular designing and screening novel HEDMs.

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1. Introduction

Nowadays, searching for novel high energy density materials (HEDMs) to meet the future demands has become one of the most activated regions and seems to be never ending because of their superior explosive performances over the currently used materials. Since synthesizing a new compound usually requires a great deal of effort and expenditure, accurate predictions of explosive performances are of significant importance in finding promising candidates for novel HEDMs. As well known, with the rapid development of computer technology and theoretical chemistry, identification of the compounds that have significant advantages over the currently used materials could be facilitated and more economical with the computer modeling and simulating. Quantitative estimation of the compounds' properties, such as heat of formation, density, detonation velocity, detonation pressure and sensitivity, would permit the selection of the most promising HEDMs' candidates for laboratory synthesis and further considerations [1]. Among which, density has been

considered as the primary physical parameter in detonation performances [2,3], because detonation velocity and pressure of the explosives increase proportionally with the packing density and square of it, respectively [3]. An increase in the solid-state density is hence desirable in terms of the amount of material that can be packed into a volume-limited warhead or propulsion configuration. Therefore, initial efforts were directed to the density prediction.

The simplest, earliest and most widely used method for the density prediction is the "group or volume additivity" method, where the molar volume is obtained by summing up the volume of appropriate atoms or functional groups [1,4]. Up to date, many researchers still often utilize this method to estimate the densities of energetic materials [5,6]. This is truly a rapid method to give the effective volume and density for a molecule. However, this method has the drawback that it cannot readily account for the molecular conformation, isomerization and crystal packing efficiency. That is, it yields the same density values for different isomers or conformations of the same compound or even for different compounds with the same functional group composition, and ignores the density differences due to crystal polymorphism. So, it is not efficient to predict the density of HEDMs by using the volume additivity method. Meanwhile, many scientists in

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various research areas have been attempting to predict the crystal packing patterns as well as the crystalline densities based on the arrays of 3D molecular structure [7–10], i.e. building packing arrangements in various space groups. However, this prediction is still a formidable task and is known to have several huge hurdles in getting the job done in a right fashion. Some applications of the packing optimization methods have been found in the area of energetic materials [9,10]. This approach seems more reliable for predicting more possible crystal structures and densities, whereas it may not be performed routinely in modeling explosives since it requires extensive computational works and takes relatively longer time and higher cost. Therefore, a novel simple approach, which can be used to rapidly and reliably assess the crystalline densities of the energetic materials, is urgently expected to come into being.

It is known that *ab initio* molecular orbital (MO) methods have been used widely now. To obtain accurate results, one often needs to perform high level calculations such as QCISD(T) (quadratic configuration interaction including single and double substitutions with a triples contribution to the energy) and MP2 (second-order Møller-Plesset) methods with electron correlation correction, but they are computationally expensive and even impossible for large systems. In contrast, density functional theory (DFT) [11,12] method, particularly the hybrid B3LYP (Becke's three-parameter nonlocal exchange functional along with the Lee-Yang-Parr nonlocal correlation functional) [13,14] functional that not only produces reliable geometries and energies but also needs less time and computer resources, has become an important and economical tool to deal with the complex electron correlation problems and been used widely.

In this paper, we report on a simple and convenient methodology for rapidly predicting the crystalline densities of energetic nitramines based on the quantum chemical computations. This group of compounds is a source of explosives or propellants that possess predominantly high energy content [15,16], and they have numerous important applications in both civilian and military fields for a long time. The DFT-B3LYP and semiempirical MO methods were chosen to perform the calculations. Results from different methods were compared, and the effects of basis sets on the molecular volumes and densities were estimated. The results may provide useful information for the molecular design and further studies of novel HEDMs.

2. Computational method

First, 45 energetic nitramines (see Table 1 or Figure IS of the Supporting Information for the structural diagrams of the molecules) generated from ChemBats3D software were fully optimized without any symmetry restrictions by the Berny method at the DFT-B3LYP level with 6-31G** basis set. To characterize the nature of the stationary points, harmonic vibrational analyses were performed subsequently on each optimized structure at the same level of theory. Since density is a very important factor to affect the detonation properties of energetic materials and sensitive to their intrinsic molecular structures, the following point must be stressed: (1) the existence of a vibrationally stable minimum on the potential

energy surface (PES) has to be examined; (2) the lowest energy isomer should be considered. The harmonic vibrational analyses demonstrated that all the optimized structures are truly local energy minima on the PES without any imaginary frequency and are the lowest energy conformers.

Then, the density of each compound was obtained from the molecular volume divided by the molecular weight, while the molecular volume of each molecule was yielded from the statistical average of 100 single-point molar volume calculations on each optimized structure. The molar volume is defined as inside a contour of 0.001 electrons/Bohr³ density and evaluated at the B3LYP/6-31G** level by using a Monte-Carlo integration as implemented in the Gaussian 03 program [17]. To evaluate the effect of basis sets on the molecular volumes and densities, we have also calculated the molecular volumes and densities of these compounds at the B3LYP level with 6-311G**, 6-31+G**, and 6-311++G** basis sets based on the B3LYP/6-31G** optimized geometries, respectively. Meanwhile, predictions on the molecular volumes and densities of the energetic nitramines were also performed with the Gaussian 03 program at the semiempirical PM3 (Parameter Method 3), AM1 (Austin Model 1), MNDO (Modified Neglect of Diatomic Differential Overlap), and MINDO/3 (Modified Intermediate Neglect of Differential Overlap 3) levels [18–21].

3. Results and discussion

3.1. DFT predictions

The compounds under study in present work are mainly cited from the references [16,22–24] and can be classified into three groups. Group I are acyclic nitramines, Group II monocyclic ones, and Group III polycyclic or cage structures. The calculated molecular volumes (V) and densities (ρ_{cal}) at the B3LYP/6-31G** level and the corresponding experimental densities (ρ_{exp}) [22–43] for the entire set of molecules were listed in Table 1. A visual comparison between experiments and predictions for different groups of compounds was shown in Fig. 1.

As can be seen from Table 1 or Fig. 1, it is evident that there are good correlations between the calculated densities and experimental data except for the compounds containing fluorine element, i.e. FIFCOM (28), FIFCUS (29) and FIFDAZ (30). A straight line with the correlation coefficient (R) 0.8911 and standard deviation (S.D.) 0.0982 was obtained on plotting the predicted densities against the experimentally determined values for the entire compounds (see Fig. 1a). However, if we eliminate three nitramines containing the element F, the linear correlation will be improved much. For example, another straight line was obtained with $R=0.9410$ and S.D.=0.0527 (Fig. 1b). Considered the calculational and experimental error, their agreement is good. In comparison with the experiment, such large differences in the predicted density values of FIFCOM, FIFCUS and FIFDAZ may be due to various factors, such as changes in the compactness of the molecules or in the intensities of electrostatic interactions, and so on. The actual crystal volume of one compound is usually occupied by the molecules (molecular volume) and the void between them. And there are intermolecular inter-

Table 1
Comparison of predicted densities (ρ_{cal}) at the B3LYP/6-31G** level and experimental data (ρ_{exp})^a

Number	Chemical name	Code design	<i>M</i> (g/mol)	<i>V</i> (cm ³ /mol)	ρ_{cal} (g/cm ³)	ρ_{exp} (g/cm ³)	$\rho_{\text{cal}}/\rho_{\text{exp}}$
Group I							
1	Nitroguanidine	NQ	104.08	65.92	1.58	1.77 [24]	0.89
2	Bis(cyanomethyl)nitramine	BCMN	140.11	94.41	1.48	1.50 [25]	0.99
3	Bis(cyanoethyl)nitramine	BCEN	168.16	122.37	1.37	1.36 [25]	1.01
4	<i>N,N'</i> -dinitrourea	DNU	150.07	81.50	1.84	1.98 [22]	0.93
5	Ethylene dinitroamine	EDNA	150.11	93.24	1.61	1.71 [24]	0.94
6	Di(2-nitroxyethyl)nitramine	DINA	240.14	141.36	1.70	1.67 [24]	1.02
7	1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane	DATH	320.22	187.88	1.70	1.72 [26]	0.99
8	1,9-Diazido-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	DATNTAN	394.27	224.97	1.75	1.67 [27]	1.05
9	1,1,1,3,6,8,8,8-Octanitro-3,6-diazaoctane	ONDO	476.22	250.25	1.90	1.88 [28]	1.01
Average							0.981
Group II							
10	1,3,3-Trinitroazetidene	TNAZ	192.10	108.21	1.78	1.84 [29]	0.97
11	1,3-Dinitro-1,3-diazacyclopentane	DNCP	162.12	98.36	1.65	1.70 [30]	0.97
12	1,3-Dinitro-1,3-diazacyclohexane	<i>m</i> -DNDC	176.14	109.47	1.61	1.57 [31]	1.03
13	1,4-Dinitro-1,4-diazacyclohexane	<i>p</i> -DNDC	176.14	109.62	1.61	1.63 [30]	0.99
14	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	222.14	124.92	1.78	1.81 [23]	0.98
15	1,3,5,5-Tetranitrohexahydropyrimidine	DNNC	266.15	146.47	1.82	1.80 [32]	1.01
16	1,3,5-Trinitro-1,3,5-triazacyclohexane-2-one	TNTACH	236.12	125.18	1.89	1.93 [23]	0.98
17	1,3-Dinitro-1,3-diazacycloheptane	<i>m</i> -DNDH	190.16	124.72	1.52	1.54 [31]	0.99
18	1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane	DNTH	220.15	129.87	1.70	1.71 [31]	0.99
19	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX (β)	296.18	157.53	1.88	1.90 [23]	0.99
20	1-(Azidomethyl)-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane	AZTC	306.23	182.30	1.68	1.70 [33]	0.99
21	1,3,3,5,7,7-Hexanitro-1,5-diazacyclooctane	HNDZ	384.20	202.16	1.90	1.88 [24]	1.01
Average							0.992
Group III							
22	1,4-Dinitrofurazano[3,4-b]piperazine	DNFP	216.04	120.81	1.79	1.83 [34]	0.98
23	1,3,4,7-Tetranitro-1,3,4,7-tetraaza bicyclo[6.5.0]nonane-2-one	TN650	322.18	168.50	1.91	1.97 [23]	0.97
24	1,3,4,6-Tetranitro-1,3,4,6-tetraaza bicyclo[5.5.0]octane-2-one	TN550	308.15	156.88	1.96	1.95 [23]	1.01
25	1,4-Dinitroglucuril	DINGU	232.13	123.63	1.88	1.96 [23]	0.96
26	1,3,4,6-Tetranitroglucuril	TNGU	322.14	158.55	2.03	2.01 [23]	1.01
27	<i>cis</i> -2,4,6,8-Tetranitro-1 <i>H</i> ,5 <i>H</i> -2,4,6,8-tetraazabicyclo[3.3.0]octane	BCHMX	294.17	156.86	1.88	1.86 [35]	1.01
28	2,6-Dinitro-3,3,3,7-tetrakis(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane	FIFCOM	476.17	201.56	2.36	1.98 [36]	1.19
29	2,4,6-Trinitro-3,3,3,7-tetrakis(trifluoromethyl)-2,4,6-tetraazabicyclo[3.3.0]octane	FIFCUS	521.17	217.50	2.40	2.11 [36]	1.14
30	2,4,6,8-Tetranitro-3,3,3,7-tetrakis(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane	FIFDAZ	566.18	232.22	2.44	2.18 [36]	1.12
31	<i>trans</i> -1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin	TNAD	322.22	179.87	1.79	1.82 [37]	0.98
32	<i>cis</i> -1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin	<i>cis</i> 1357TNAD	322.22	179.57	1.79	1.79 [38]	1.00
33	<i>trans</i> -1,3,5,7-Tetranitro-1,3,5,7-tetraazadecalin	<i>trans</i> 1357TNAD	322.22	181.41	1.78	1.75 [38]	1.02
34	1,1',3,3'-Tetranitro-4,4'-biimidazolidine	(<i>r,r</i>)-TNBI	322.22	185.59	1.74	1.71 [39]	1.02
35	1,3,7,9-Tetranitro-1,3,7,9-tetraazaspiro[4.5]decane	TNSD	322.22	178.98	1.80	1.71 [39]	1.05
36	2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane	TNSU	336.25	191.11	1.76	1.74 [40]	1.01
37	1,3,5,7-Tetranitro-3,7-diazabicyclo[3.3.1]nonane	TNDBN	306.10	173.17	1.77	1.66 [41]	1.07
38	Tetranitropropanediurea	TNPD	336.16	171.70	1.96	1.98 [22]	0.99
39	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza tricyclo[7.3.0.0]dodecane-5,11-dione	HHTDD	468.21	230.17	2.03	2.07 [22]	0.98
40	Octahydro-1,3,4,6-tetranitro-3aa,3bp,6ap,6ba-cyclobutane[1,2-d:3,4-d']diimidazole	TNTriCB	320.20	175.60	1.82	1.83 [42]	0.99
41	Octahydro-1,3,4,6-tetranitro-3aa,3bp,6ap,6ba-cyclobutane[1,2-d:3,4-d']diimidazole-2,5-dione	TNCB	348.17	178.46	1.95	1.99 [22]	0.98
42	1,1'-Dinitro-3,3'-azo-1,2,4-triazole	N-DNAT	254.06	141.15	1.80	1.81 [22]	0.99
43	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	262.15	136.85	1.92	1.99 [43]	0.96
44	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	HNIW (ϵ)	438.23	218.89	2.00	2.04 [23]	0.98
45	Hexanitrohexaazadamantane	HANA	412.19	198.04	2.08	2.10 [23]	0.99
Average							1.017
Total average							1.003

^a References for experimental values are given in the brackets.

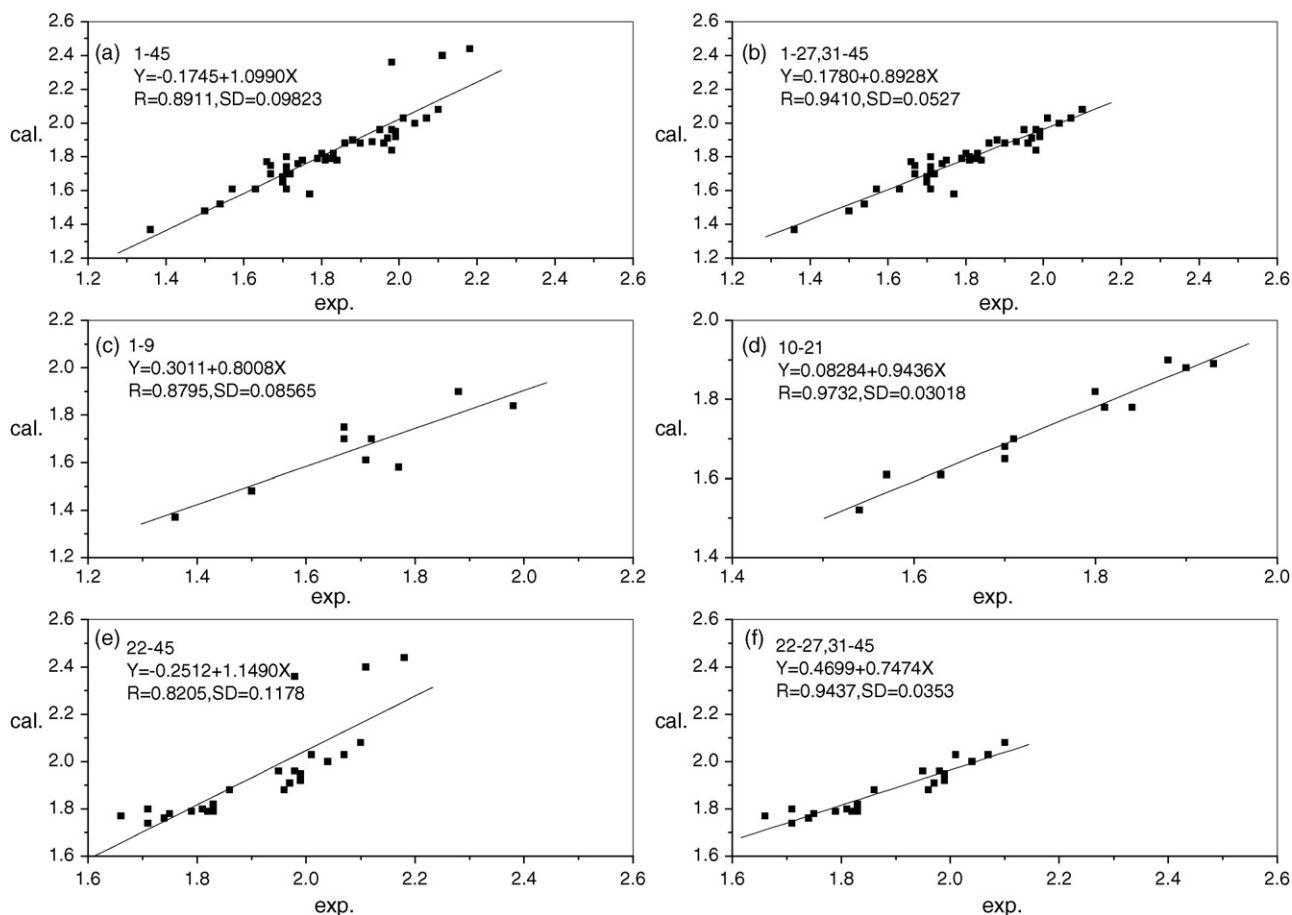


Fig. 1. Comparison of the experimental and predicted densities at the B3LYP/6-31G** level for: (a) the entire set of molecules; (b) all molecules except three compounds with the element F; (c) acyclic nitramines; (d) monocyclic nitramines; (e) polycyclic nitramines; (f) polycyclic nitramines except three compounds with the element F.

actions in the crystal, but such interactions are not present in the DFT calculations applied here. Since the F atoms have strong electronegativity, there may be stronger electrostatic repulsions rather than attractions between molecules in these solids. So, these polar molecules are less closely packed in the experimental measurements (there are vacancies in the actual bulk) than in the theoretical calculations. Consequently, this leads to larger volumes and smaller measured densities than the calculated results. It is also noted that in comparison with the experimental data, somewhat smaller density values are obtained for the acyclic molecules NQ (1), DNU (4) and EDNA (5). Similar explanations are also true for the cyclic ones. These molecules are more closely packed in the solid state than in the calculations because of the strong intra- and intermolecular hydrogen bonds in the bulk. Since such interactions are partially described in the DFT calculations applied here, our calculations predict larger molecular volume and smaller density values than the experiments.

Separate analyses performed on the acyclic (Group I, 1–9), monocyclic (Group II, 10–21), and polycyclic nitramines (Group III, 22–45) are shown in Fig. 1c–f, respectively. One could find that the predicted densities for the monocyclic nitramines are in good agreement with the experiments with $R = 0.9732$, $S.D. = 0.0302$, and those predicted for the polycyclic nitramines except three compounds containing F atoms

are comparable with the experimental ones with $R = 0.9437$, $S.D. = 0.0353$. But, the correlation between the predicted and experimental values for the acyclic nitramines is worse, with $R = 0.8795$, $S.D. = 0.0856$. Therefore, it can be concluded from above discussion that this method could reliably predict the crystal densities of the energetic nitramines at the B3LYP/6-31G** level and is especially suitable for predicting the solid-state densities of the monocyclic nitramines. This can be also drawn directly from the $\rho_{\text{cal-to-}}\rho_{\text{exp}}$ ratios for different groups of compounds (see Table 1).

Next, we consider the effects of basis sets on the molecular volumes and densities of the systems. First, a similar finding emerges from comparison of the results at the B3LYP level with 6-311G**, 6-31+G**, and 6-311++G** basis sets, respectively, in Table 2. As a whole, the correlation between the predicted and experimental densities for the monocyclic nitramines is better than those for the acyclic and polycyclic ones at different levels, and there are larger deviations from the experimental values for the compounds with the fluorine element, too. This can also be seen from the $\rho_{\text{cal-to-}}\rho_{\text{exp}}$ ratios in Table 2 or the linear regression analyses listed in Table 4. Second, the basis sets have a little effect on the volume and density calculations. On the whole, if a larger basis set is chosen, larger molecular volume and smaller density will be correspondingly obtained. This

Table 2
Effects of basis sets on the molecular volumes (V) and densities (ρ_{cal}) calculated at the B3LYP level^a

Number	V (cm ³ /mol)			ρ_{cal} (g/cm ³)			$\rho_{\text{cal}}/\rho_{\text{exp}}$		
	6-311G**	6-31+G**	6-311++G**	6-311G**	6-31+G**	6-311++G**	6-311G**	6-31+G**	6-311++G**
Group I									
1	67.29	69.11	69.40	1.55	1.51	1.50	0.88	0.85	0.85
2	97.45	95.16	98.24	1.44	1.47	1.43	0.96	0.98	0.95
3	123.34	124.19	125.27	1.36	1.35	1.34	1.00	0.99	0.99
4	81.93	84.48	85.72	1.83	1.78	1.75	0.92	0.90	0.88
5	94.93	96.92	95.91	1.58	1.55	1.57	0.92	0.91	0.92
6	144.71	148.08	147.51	1.66	1.62	1.63	0.99	0.97	0.98
7	189.97	189.31	190.78	1.69	1.69	1.68	0.98	0.98	0.98
8	228.56	232.88	232.66	1.73	1.69	1.69	1.04	1.01	1.01
9	252.60	255.73	257.32	1.89	1.86	1.85	1.00	0.99	0.98
Average							0.966	0.954	0.949
Group II									
10	108.85	111.00	110.99	1.76	1.73	1.73	0.96	0.94	0.94
11	98.46	98.56	100.46	1.65	1.64	1.61	0.97	0.96	0.95
12	113.06	111.52	113.42	1.56	1.58	1.55	0.99	1.01	0.99
13	113.85	113.93	114.61	1.55	1.55	1.54	0.95	0.95	0.94
14	124.38	125.93	126.09	1.79	1.76	1.76	0.99	0.97	0.97
15	147.21	147.35	146.65	1.81	1.81	1.81	1.01	1.01	1.01
16	127.24	129.57	128.65	1.86	1.82	1.84	0.96	0.94	0.95
17	124.53	123.91	125.52	1.53	1.53	1.51	0.99	0.99	0.98
18	132.45	130.49	131.93	1.66	1.69	1.67	0.97	0.99	0.98
19	162.79	166.08	167.41	1.82	1.78	1.77	0.96	0.94	0.93
20	183.80	183.74	185.10	1.67	1.67	1.65	0.98	0.98	0.97
21	205.71	203.96	205.71	1.87	1.88	1.87	0.99	1.00	0.99
Average							0.977	0.973	0.967
Group III									
22	121.58	121.38	121.42	1.78	1.78	1.78	0.97	0.97	0.97
23	170.99	171.91	174.34	1.88	1.87	1.85	0.95	0.95	0.94
24	159.51	161.85	163.26	1.93	1.90	1.89	0.99	0.97	0.97
25	125.77	127.48	127.90	1.85	1.82	1.81	0.94	0.93	0.92
26	162.37	163.87	160.75	1.98	1.97	2.00	1.02	1.02	1.03
27	158.40	161.19	164.56	1.86	1.82	1.79	1.00	0.98	0.96
28	204.20	209.53	207.61	2.33	2.27	2.29	1.18	1.15	1.16
29	220.89	225.73	222.62	2.36	2.31	2.34	1.12	1.09	1.11
30	239.54	239.80	240.22	2.36	2.36	2.36	1.08	1.08	1.08
31	182.13	182.09	183.84	1.77	1.77	1.75	0.97	0.97	0.96
32	187.15	184.23	184.90	1.72	1.75	1.74	0.96	0.98	0.97
33	182.06	185.94	181.98	1.77	1.73	1.77	1.01	0.99	1.01
34	181.00	186.56	186.87	1.78	1.73	1.72	1.04	1.01	1.01
35	180.02	183.61	184.43	1.79	1.75	1.75	1.05	1.02	1.02
36	196.04	198.60	198.51	1.72	1.69	1.69	0.99	0.97	0.97
37	174.59	179.93	179.05	1.75	1.70	1.71	1.05	1.02	1.03
38	173.66	175.79	178.68	1.94	1.91	1.88	0.98	0.96	0.95
39	229.36	234.34	236.62	2.04	2.00	1.98	0.99	0.97	0.96
40	177.61	178.25	181.76	1.80	1.80	1.76	0.98	0.98	0.96
41	181.87	181.92	183.67	1.91	1.91	1.90	0.96	0.96	0.95
42	143.92	143.67	145.83	1.77	1.77	1.74	0.98	0.98	0.96
43	133.42	140.62	141.40	1.96	1.86	1.85	0.98	0.93	0.93
44	218.85	221.23	221.03	2.00	1.98	1.98	0.98	0.97	0.97
45	204.53	202.47	204.83	2.02	2.04	2.01	0.96	0.97	0.96
Average							1.005	0.992	0.990
Total average							0.990	0.980	0.975

^a Volume calculations are based on the B3LYP/6-31G** optimized geometries.

Table 3
Molecular volumes (V) and densities (ρ_{cal}) obtained from the semiempirical MO calculations

Number	V (cm ³ /mol)				ρ_{cal} (g/cm ³)				$\rho_{\text{cal}}/\rho_{\text{exp}}$			
	PM3	AM1	MNDO	MINDO/3	PM3	AM1	MNDO	MINDO/3	PM3	AM1	MNDO	MINDO/3
Group I												
1	57.68	55.94	55.80	57.76	1.80	1.86	1.87	1.80	1.02	1.05	1.05	1.02
2	79.84	79.50	79.98	79.07	1.75	1.76	1.75	1.77	1.17	1.17	1.17	1.18
3	106.75	103.00	106.84	107.73	1.58	1.63	1.57	1.56	1.16	1.20	1.16	1.15
4	67.46	64.62	64.73	65.90	2.22	2.32	2.32	2.28	1.12	1.17	1.17	1.15
5	82.01	77.91	79.61	78.22	1.83	1.93	1.89	1.92	1.07	1.13	1.10	1.12
6	118.59	116.6	121.87	123.81	2.02	2.06	1.97	1.94	1.21	1.23	1.18	1.16
7	161.23	156.46	161.54	159.99	1.99	2.05	1.98	2.00	1.15	1.19	1.15	1.16
8	200.42	192.19	197.37	196.50	1.97	2.05	2.00	2.01	1.18	1.23	1.20	1.20
9	204.36	204.48	211.31	205.97	2.33	2.33	2.25	2.31	1.24	1.24	1.20	1.23
Average									1.147	1.178	1.153	1.152
Group II												
10	90.38	88.24	88.93	89.20	2.13	2.18	2.16	2.15	1.16	1.18	1.17	1.17
11	85.14	82.36	85.76	85.31	1.90	1.97	1.89	1.90	1.12	1.16	1.11	1.12
12	96.24	95.22	98.15	96.58	1.83	1.85	1.79	1.82	1.17	1.18	1.14	1.16
13	97.77	93.33	96.77	96.69	1.80	1.89	1.82	1.82	1.10	1.16	1.12	1.12
14	107.09	104.54	103.94	104.71	2.07	2.12	2.14	2.12	1.14	1.17	1.18	1.17
15	123.50	118.82	122.88	122.91	2.16	2.24	2.17	2.17	1.20	1.24	1.20	1.20
16	105.94	102.07	104.54	105.79	2.23	2.31	2.26	2.23	1.16	1.20	1.17	1.16
17	108.42	105.46	107.53	107.94	1.75	1.80	1.77	1.76	1.14	1.17	1.15	1.14
18	113.44	112.56	113.50	113.88	1.94	1.96	1.94	1.93	1.13	1.14	1.13	1.13
19	142.17	138.85	140.14	138.16	2.08	2.13	2.11	2.14	1.09	1.12	1.11	1.13
20	160.98	150.62	154.69	155.08	1.90	2.03	1.98	1.97	1.12	1.20	1.16	1.16
21	174.61	167.31	172.94	172.50	2.20	2.30	2.22	2.23	1.17	1.22	1.18	1.18
Average									1.142	1.178	1.152	1.153
Group III												
22	103.80	99.92	101.98	101.27	2.08	2.16	2.12	2.13	1.14	1.18	1.16	1.16
23	144.56	141.74	146.17	145.49	2.23	2.27	2.20	2.21	1.13	1.15	1.12	1.12
24	133.89	130.95	133.47	132.38	2.30	2.35	2.31	2.33	1.18	1.21	1.18	1.19
25	108.38	102.76	106.01	105.04	2.14	2.26	2.19	2.21	1.09	1.15	1.12	1.13
26	136.00	128.81	132.71	131.01	2.37	2.50	2.43	2.46	1.18	1.24	1.21	1.22
27	134.21	130.91	139.33	133.96	2.19	2.25	2.11	2.20	1.18	1.21	1.13	1.18
28	170.94	167.80	172.00	159.18	2.79	2.84	2.77	2.99	1.41	1.43	1.40	1.51
29	186.91	182.10	183.91	167.60	2.79	2.86	2.83	3.11	1.32	1.36	1.34	1.47
30	199.61	191.11	196.21	176.00	2.84	2.96	2.89	3.22	1.30	1.36	1.33	1.48
31	160.60	152.31	161.52	156.21	2.01	2.12	1.99	2.06	1.12	1.18	1.05	1.14
32	157.78	151.55	160.78	156.36	2.04	2.13	2.00	2.06	1.15	1.20	1.12	1.16
33	158.43	153.19	155.51	156.15	2.03	2.10	2.07	2.06	1.16	1.20	1.18	1.18
34	159.22	156.83	157.93	160.92	2.02	2.05	2.04	2.00	1.18	1.20	1.19	1.17
35	157.01	152.02	161.76	157.23	2.05	2.12	1.99	2.05	1.21	1.25	1.17	1.21
36	170.11	163.05	171.80	170.17	1.98	2.06	1.96	1.98	1.14	1.18	1.13	1.14
37	154.94	146.54	150.03	150.87	1.98	2.09	2.04	2.03	1.19	1.26	1.23	1.22
38	148.54	142.07	142.67	141.82	2.26	2.37	2.36	2.37	1.14	1.20	1.19	1.20
39	197.28	190.00	194.04	191.81	2.37	2.46	2.41	2.44	1.14	1.19	1.16	1.18
40	154.00	151.05	150.39	150.37	2.08	2.12	2.13	2.13	1.14	1.16	1.16	1.16
41	150.03	148.79	150.37	150.94	2.32	2.34	2.32	2.31	1.17	1.18	1.17	1.16
42	119.23	116.32	116.74	116.45	2.13	2.18	2.18	2.18	1.18	1.20	1.20	1.20
43	116.03	116.08	115.19	114.06	2.26	2.26	2.28	2.30	1.14	1.14	1.15	1.16
44	186.74	184.50	186.42	180.62	2.35	2.38	2.35	2.43	1.15	1.17	1.15	1.19
45	169.45	163.47	164.60	164.31	2.43	2.52	2.50	2.51	1.16	1.20	1.19	1.20
Average									1.179	1.217	1.185	1.214
Total average									1.163	1.199	1.170	1.185

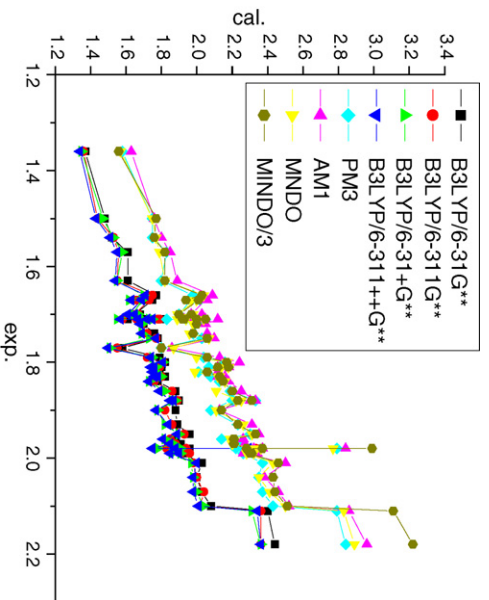


Fig. 2. Comparison of the calculated densities by DFT-B3LYP and semiempirical MO methods along with the experimental data.

can be attributed to the fact that the electrons occupy more space when the selected basis set becomes larger. And the correlation between the predicted and experimental densities decreases with the basis set increases, which can also be observed from the $\rho_{\text{calc}}/\rho_{\text{exp}}$ ratios or the linear regression analyses ranging from the B3LYP/6-31G** level to B3LYP/6-311++G** level. Therefore, one can draw a conclusion that it is dependable and economical to predict the crystal densities of the energetic nitramines at the B3LYP/6-31G** level.

Previously, an approach to ab initio crystal structure and density prediction by packing optimization has been developed and reported for the organic nitramines [9c], which was employed to predict the crystal structures and densities of three known polymorphs and other possible packings of HMX, and the possible crystal structures and densities of eight isomeric azanitroadamantanes and wurtzitanes. Compared with their results, it can be found that our predicted density for the β -HMX is close to the previous study and the experiment although we do not consider the crystal packing and intermolecular potential. This further demonstrated that our proposed methodology based on the DFT calculations is suitable for reliably and rapidly predicting the crystalline densities of the organic nitramines.

3.2. Comparison of DFT and semiempirical results

Semiempirical MO methods could give the molecular volumes more rapidly than the DFT methods, but their validity is sometimes limited. Table 3 lists the molecular volumes and densities predicted for these studied energetic compounds by four semiempirical MO methods (PM3, AM1, MNDO, and MINDO/3). Fig. 2 shows the overall relationships between the experimental densities and the calculated values by the DFT-B3LYP and semiempirical MO methods. In comparison with the values predicted by the DFT-B3LYP methods, it is obvious that semiempirical MO methods all greatly overestimate the densities for all the organic nitramines. However, it is interesting to note that the semiempirical MO and DFT-B3LYP calculations keep the same tendencies in predicting the densities of the

Table 4
Correlation between the predicted and experimental densities^a

Method	Total (1–45) ^b	Total' (1–27, 31–45)	Group I (1–9)	Group II (10–21)	Group III (22–45)	Group III' (22–27, 31–45)
B3LYP/6-31G**	$Y = -0.1745 + 1.0990X$ $R = 0.8911$, S.D. = 0.0982	$Y = 0.1780 + 0.8928X$ $R = 0.9410$, S.D. = 0.0527	$Y = 0.3011 + 0.8008X$ $R = 0.8795$, S.D. = 0.0856	$Y = 0.0828 + 0.9436X$ $R = 0.9732$, S.D. = 0.0302	$Y = -0.2512 + 1.1490X$ $R = 0.8205$, S.D. = 0.1178	$Y = 0.4699 + 0.7474X$ $R = 0.9437$, S.D. = 0.0353
B3LYP/6-311G**	$Y = -0.1591 + 1.0777X$ $R = 0.8920$, S.D. = 0.0958	$Y = 0.1580 + 0.8919X$ $R = 0.9326$, S.D. = 0.0566	$Y = 0.2472 + 0.8195X$ $R = 0.8754$, S.D. = 0.0894	$Y = 0.0926 + 0.9242X$ $R = 0.9680$, S.D. = 0.0325	$Y = -0.1611 + 1.0894X$ $R = 0.8163$, S.D. = 0.1135	$Y = 0.4908 + 0.7256X$ $R = 0.9231$, S.D. = 0.0407
B3LYP/6-31+G**	$Y = -0.1051 + 1.0374X$ $R = 0.8895$, S.D. = 0.0935	$Y = 0.2141 + 0.8507X$ $R = 0.9262$, S.D. = 0.0568	$Y = 0.3704 + 0.7330X$ $R = 0.8466$, S.D. = 0.0911	$Y = 0.2819 + 0.8118X$ $R = 0.9292$, S.D. = 0.0437	$Y = -0.2118 + 1.1032X$ $R = 0.8423$, S.D. = 0.1039	$Y = 0.4209 + 0.7509X$ $R = 0.9517$, S.D. = 0.0326
B3LYP/6-311++G**	$Y = -0.1427 + 1.0536X$ $R = 0.8788$, S.D. = 0.1004	$Y = 0.2010 + 0.8526X$ $R = 0.9189$, S.D. = 0.0600	$Y = 0.3625 + 0.7325X$ $R = 0.8406$, S.D. = 0.0933	$Y = 0.1279 + 0.8936X$ $R = 0.9423$, S.D. = 0.043	$Y = -0.126 + 1.1022X$ $R = 0.8135$, S.D. = 0.1160	$Y = 0.4926 + 0.7133X$ $R = 0.9229$, S.D. = 0.0401
PM3	$Y = -0.3726 + 1.3675X$ $R = 0.8939$, S.D. = 0.1203	$Y = 0.0240 + 1.1352X$ $R = 0.9334$, S.D. = 0.0716	$Y = 0.1082 + 1.0823X$ $R = 0.8555$, S.D. = 0.1294	$Y = -0.1268 + 1.2143X$ $R = 0.9470$, S.D. = 0.0558	$Y = -0.5917 + 1.4887X$ $R = 0.8428$, S.D. = 0.1399	$Y = 0.1921 + 1.0509X$ $R = 0.9419$, S.D. = 0.0505
AM1	$Y = -0.3811 + 1.4087X$ $R = 0.9001$, S.D. = 0.1196	$Y = 0.0286 + 1.169X$ $R = 0.9384$, S.D. = 0.0706	$Y = 0.0768 + 1.1336X$ $R = 0.8948$, S.D. = 0.1118	$Y = -0.1568 + 1.2690X$ $R = 0.9396$, S.D. = 0.0626	$Y = -0.5501 + 1.5042X$ $R = 0.8399$, S.D. = 0.1430	$Y = 0.2878 + 1.0373X$ $R = 0.9284$, S.D. = 0.0559
MNDO	$Y = -0.4753 + 1.4335X$ $R = 0.9120$, S.D. = 0.1131	$Y = -0.0846 + 1.2049X$ $R = 0.9493$, S.D. = 0.0655	$Y = -0.0246 + 1.1679X$ $R = 0.9369$, S.D. = 0.0861	$Y = -0.2653 + 1.3057X$ $R = 0.9557$, S.D. = 0.0544	$Y = -0.7497 + 1.5808X$ $R = 0.8565$, S.D. = 0.1402	$Y = 0.0286 + 1.1468X$ $R = 0.9170$, S.D. = 0.0672
MINDO/3	$Y = -0.8137 + 1.6346X$ $R = 0.8667$, S.D. = 0.1651	$Y = -0.1465 + 1.2452X$ $R = 0.9486$, S.D. = 0.0682	$Y = 0.0030 + 1.1509X$ $R = 0.8947$, S.D. = 0.1136	$Y = -0.2223 + 1.2807X$ $R = 0.9629$, S.D. = 0.0486	$Y = -1.3464 + 1.9215X$ $R = 0.8109$, S.D. = 0.2041	$Y = -0.0254 + 1.1873X$ $R = 0.9419$, S.D. = 0.0571

^a R and S.D. denote the correlation coefficient and standard deviation, respectively.

^b 1–45 present the serial number of the compounds listed in Table 1.

energetic compounds. Namely, the correlation between the predicted and experimental densities for the Group II (monocyclic nitramines) is also better than those for the Group I (acyclic ones) and Group III (polycyclic ones) by different semiempirical methods, and there are larger deviations from the experimental values for the compounds with the element F, too. All of these can be realized from the $\rho_{\text{cal}}/\rho_{\text{exp}}$ ratios in Table 3 or the linear regression analyses in Table 4.

In addition, it is evident that all the densities calculated by the semiempirical MO methods are systematically much larger than the experimental data. This agrees well with the previous study of Klapotke and Ang [22]. They estimated the maximum crystalline densities for a number of nitramines and some other energetic materials by utilizing the semiempirical PM3 method, and suggested a relationship between the maximum crystalline densities and predicted values for the energetic materials ($\rho_{\text{max}} = 0.86/\rho_{\text{PM3}}$). Similarly, in our work the correlations between the experiments and predictions by the semiempirical methods can be also expressed as follows: $\rho_{\text{exp}} = 0.86/\rho_{\text{PM3}}$, $\rho_{\text{exp}} = 0.83/\rho_{\text{AM1}}$, $\rho_{\text{exp}} = 0.86/\rho_{\text{MNDO}}$ and $\rho_{\text{exp}} = 0.84\rho_{\text{MINDO/3}}$, respectively. These are in good agreement with Klapotke's work, but it also suggests that the errors of ρ_{cal} predicted by the semiempirical MO methods relative to ρ_{exp} are large. Thus, it may be not appropriate and accurate for predicting the crystal densities of HEDMs by using the semiempirical MO methods.

In conclusion, the B3LYP/6-31G** method is recommended as the most suitable approach for predicting the crystalline densities of the energetic nitramines. Based on the predicted densities and heats of formation, it is possible to further estimate the detonation velocity, detonation pressure, and other detonation characteristics of the energetic compounds by the computer codes (such as CHEETAH and TIGER [44]) or the other empirical correlations (such as the Kamlet–Jacobs formula [3]), which can effectively screen target structures for further synthesis and study. Recently, this procedure has been successfully employed to study and design a series of novel HEDMs among the spiro and cage nitramines as well as other energetic systems [45–48]. The calculated results agree well with the available experimental data and suggest some potential candidates of HEDMs with superior detonation performances compared with the benchmarks such as TNT, RDX and HMX.

4. Conclusions

The present paper reports an efficient and convenient method for rapidly and reliably predicting the crystalline densities of energetic nitramines based on the quantum chemical calculations. The system under study consists of acyclic, monocyclic, and polycyclic molecules. Predictive capacity of this method was demonstrated by experimental verification of the calculated data, which seems to be of essential interest and significance. Comparisons between the calculated and experimental densities suggest that B3LYP/6-31G** is most accurate and economical for predicting the solid-state densities of the organic nitramines, especially for the monocyclic ones, but the densities of the compounds containing the fluorine element are all overestimated by the quantum chemical calculations. The densities predicted

by the semiempirical MO methods are all systematically larger than the experimental ones. The calculations also show that if a larger basis set is selected, it will expend more CPU time, meanwhile larger molecular volume and smaller density will be obtained. Furthermore, based on the predicted densities it is possible to further estimate the detonation velocity, detonation pressure, and other detonation characteristics of the energetic compounds, and to rapidly and effectively screen promising candidates of HEDMs for further consideration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2006.06.135.

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