



Novel method for predicting densities of polynitro arene and polynitro heteroarene explosives in order to evaluate their detonation performance

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ABSTRACT

The paper presents a new method for prediction of crystal densities of polynitro arenes and polynitro heteroarenes as two important classes of energetic compounds. The novel method assumes that densities of these compounds with general formula $C_aH_bN_cO_d$ can be easily obtained from their molecular structures. Two specific structural parameters for polynitro arenes and polynitro heteroarenes, separately, in the new method can increase or decrease the predicted values. The predicted results show that this method gives reliable predictions of crystal densities as compared to well-developed group additivity methods for different polynitro arene and polynitro heteroarene explosives with complex molecular structures.

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1. Introduction

Density and heat of formation are two key properties of explosives for an explosive technologist to achieve high detonation performance. To calculate detonation pressure and velocity of a new explosive, computer codes such as CHEETAH [1] or various empirical methods [2,3] usually use density and heat of formation of explosives. An increase in oxygen content and heat of formation of an explosive generally increases its sensitivity as well as its performance. Increasing the density should do more to improve the performance without increasing the sensitivity because the Chapman–Jouguet (C–J) pressure is proportional to the square of initial density [4]. Further investigations show that the performance of an explosive is greatly sensitive to its crystalline density, but somewhat less sensitive to its heat of formation [5].

Some different methods exist to estimate the density of compounds. Quantum chemistry programs and group additivity methods are two broad categories for determination of density. A powerful simulation methodology known as *ab initio* crystal prediction can be used to assess the ability of a generalized model of $C_aH_bN_cO_d$ intermolecular interactions [6]. Group additivity methods, such as Tarver's method [7], are the other convenient methods

for estimating the density of energetic materials which are based on summing up the volume of each atom or molecular fragment. A simple approach has been recently introduced to quick estimation of densities of nitroaromatic explosive compounds [8]. Since the density of an energetic material is the primary physical parameter in detonation performances [2,3], reliable prediction of the density for estimating the performance of new high-energy materials has received a great amount of interest. There are ongoing research programs worldwide to develop new explosives with higher performance or enhanced insensitivity to thermal or shock insults. In recent years, synthesis of polynitro arenes and polynitro heteroarenes has special importance to chemist because some of them have relatively high densities and suitable heats of formation. Thus, these compounds can be used as thermally stable, high-performance, melt-castable and insensitive high explosives [9–12]. The purpose of this work is to predict a reliable simple correlation for predicting crystal densities of polynitro arenes and polynitro heteroarenes. The predicted results for some polynitro arenes are compared with Tarver's method [7] for somewhere this group additivity method can be applied. The new method is also compared against experimental results, new Ammon's group additivity method [13] and previous work [8] for further explosives. Moreover, it is shown here how this method can predict quick reliable results of new explosives with complex molecular structures. The most important aspect of the present work is that only two specific structural parameters, separately, in the new method can increase or decrease the predicted values.

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2. Theory

2.1. Prediction of densities by group additivity methods

The group additivity approach of density prediction was used by Exner [14] to consolidate the idea of additivity of constituent volumes. Exner [14] estimated densities for most liquid explosives to within a standard deviation of 0.008 g/cm³. His method is invalid only for liquids with extremely branched chains or directly bonded functional groups. Nielsen [15] extended Exner's method in order to include constituent volumes related to multi-numbered ring systems and chemical entities found in explosives. Negative and positive contributions to the molar volume can be found for 10–18-member ring and all other ring systems, respectively.

Immirzi and Perini [16] used a 500-structure database and restricted cyclic compounds to those materials containing benzene and naphthalene rings. They defined a set of 15 constituent volumes that are basically atomic volumes. Tarver [7] used a database of 188 explosives and related compounds and defined a different set of constituent volumes than those of previous works. The mentioned empirical methods are concerned with estimating a compound's molar volume (cm³/mol) or equivalently its crystal volume in which contributions from actual volume occupied by molecular volume or the voids of molecules are included. Kitiagorodsky [17] used the volume of each atom to estimate the molecular volume through an empirically determined van der Waal's radius.

Stine [18] employed "error-free" crystal structure database to determine 34 atomic volumes for C, H, N, O and F. Since Stine's method [18] is based on a large number of empirical data, the confidence limits may be determined more accurately. Ammon and Mitchell [19] determined a new group additivity database to provide atom and functional volumes for calculation of solid state density. They developed 78 parameters corresponding to each groups or atoms by examining more than 11,000 crystal structure data. Two further volume additivity works have been reported, which are based on single element volumes [20] or molecular salts and hydrates [21]. Ammon [13] has also expanded previous list of Ammon and Mitchell [19] for atom and group volumes and introduced the concept of the atom-code.

2.2. Quantum mechanical investigations

Some quantum mechanical investigations have been reported over recent years that used different approaches for prediction of crystal densities [22,23]. *Ab initio* crystal structure prediction is a molecular simulation capability of particular importance in developments of energetic materials. Since this type of calculation allows the prediction of crystal density of energetic solids, it has the potential to significantly enhance and optimize design and development of advanced energetic materials.

The success of *ab initio* computation is dependent on the quality of the model used to describe intermolecular interactions among the atoms in the crystals. In recent years, the Gaussian 98 program [24] with appropriate basis set can be used for this purpose. Some representative examples are given here. Rice and Sorescu [6] used a generalized C_aH_bN_cO_d intermolecular interaction potential, which is denoted as the SRT mode. To use the SRT interaction potential, they subjected a series of C_aH_bN_cO_d crystals with this model that are representative of different classes of explosives. Wang et al. [25] employed the DFT-B3LYP method [26] with the basis set 6-31G* to fully optimize molecular geometries of some polynitro arenes. Since vibrational analysis of optimized molecular geometries indicated that all structures were stable, the average molecular volume and theoretical density were estimated using Monte-Carlo method based on 0.001 electrons/bohrs³ density space [25]. Kim

and coworkers [27] have also recently predicted the densities of high energetic molecules in the solid state with a simplified scheme based on molecular surface electrostatic potentials.

2.3. Some of the other models for prediction of density of energetic compounds

Cho et al. [5] introduced an interesting approach to quick density prediction based on a holographic quantitative structure–activity relationship (HQ SAR) developed with 449 selected energetic compounds. They have left out 49 molecules to utilize as a test set. They carefully selected some compounds for a test set so that the density distribution of which was similar to that of total data set. They have shown that the predicted results from the Stine's method [18] and the Ammon's method [13] have large deviations in some energetic materials.

It was found that elemental composition of nitroaromatic, acyclic and cyclic nitramines, nitroaliphatic compounds can be used for calculation of density [8,28]. The introduced core correlation for C_aH_bN_cO_d nitroaromatic explosive compounds is much simple to use for complex molecular structures and has the following form [8]:

$$\rho'_0 = 10.57a' + 0.127b' + 30.38c' + 35.19d' \quad (1)$$

where *a'*, *b'*, *c'* and *d'* are the number of carbon, hydrogen, nitrogen and oxygen divided by molecular weight of explosive, ρ'_0 is the core crystal density of explosive that can be corrected for some specific classifications of nitroaromatic compounds. The predicted results for some well-known nitroaromatic explosives, where Tarver's method can be used, show that the reliability of this method is less than Traver's method [8].

3. Results and discussion

Detonation pressure is one of the important detonation parameters in predicting the explosive performance, which can be calculated by using the following equation [29] for ideal and some of less ideal C_aH_bN_cO_dF_eCl_f explosives:

$$P = 15.9\alpha(MQ)^{1/2}\rho_0^2 - 11.2 \quad (2)$$

where *P* is detonation pressure in kbar, α is the number of moles of gaseous products of detonation per gram of explosive, *M* is the average molecular weight of gaseous products, ρ_0 is loading density and *Q* is the estimated heat of detonation. The heat of detonation can be determined from the heat of formation of reactants and decomposition products of the explosive through the relation:

$$Q \cong - \frac{\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive})}{\text{Formula weight of explosive}} \quad (3)$$

However, detonation pressure is indirectly proportional to the square root of condensed phase of formation of explosive. Meanwhile, it is directly proportional to the square of initial density. Thus, the performance of explosive is greatly sensitive to the density values.

Since more accurate prediction of the crystal density of new explosives are of significant importance for reliable prediction of explosive performance development of new methods, it was found that suitable combination of elemental composition and some structural parameters polynitro arenes and polynitro heteroarenes can be used for this purpose. The study of crystal densities for various polynitro arenes and polynitro heteroarenes has shown that it is possible to correlate crystal density with some specific structural parameters [8,28]. The results show that elemental compositions as

Table 1

Density estimation for 25 well-known solid polynitro arenes by new method, previous work [8] and Tarver's method [7].

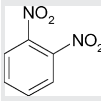
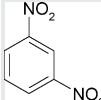
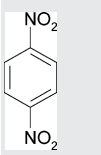
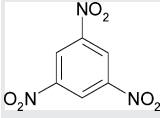
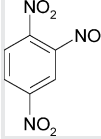
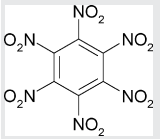
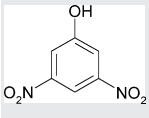
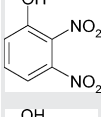
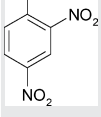
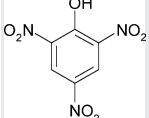
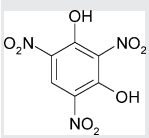
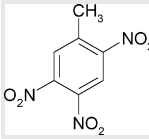
Explosive	Measured density (g/cm ³) ^a	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Tarver's method	%Error
	1.565	1.561	0.226	1.580	0.962	1.572	0.447
	1.575	1.561	0.859	1.580	0.314	1.572	0.190
	1.625	1.632	-0.417	1.580	2.766	1.572	3.262
	1.688	1.709	-1.265	1.719	1.816	1.709	1.244
	1.73	1.709	1.193	1.719	0.656	1.709	1.214
	1.988	1.994	-0.293	1.919	3.452	1.954	1.710
	1.702	1.689	0.747	1.683	1.129	1.658	2.585
	1.681	1.689	-0.493	1.683	0.106	1.658	1.368
	1.683	1.689	-0.373	1.683	0.013	1.658	1.485
	1.763	1.780	-0.986	1.788	1.175	1.778	0.851
	1.829	1.847	-0.969	1.814	0.893	1.843	0.765
	1.62	1.647	-1.647	1.660	2.491	1.636	0.988

Table 1 (Continued)

Explosive	Measured density (g/cm ³) ^a	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Tarver's method	%Error
	1.604	1.591	0.792	1.609	0.301	1.577	1.683
	1.654	1.647	0.442	1.660	0.384	1.636	1.088
	1.59	1.591	-0.082	1.609	1.184	1.577	0.818
	1.867	1.818	2.626	1.821	2.450	1.867	0.000
	1.762	1.730	1.791	1.739	1.284	1.775	0.738
	1.837	1.819	0.968	1.792	2.423	1.838	0.054
	1.938	1.906	1.659	1.955	0.889	1.897	2.116
	1.48	1.467	0.885	1.563	5.605	1.528	3.243
	1.69	1.709	-1.145	1.719	1.695	1.707	1.006
rms deviation			1.120		2.003		1.560

^a Measured densities were obtained from Ref. [7].

well as positive and negative contributions of some specific structural parameters are important factors which can be written as:

$$\rho = y_1 + y_2a' + y_3b' + y_4c' + y_5d' + y_6C_{PG} + y_7C_{NG} \quad (4)$$

where a' , b' , c' and d' are the number of carbon, hydrogen, nitrogen and oxygen divided by molecular weight of explosive, C_{PG} and C_{NG} are the positive and the negative contributions of some specific structural parameters for specific functional group, y_1 – y_7 are adjustable parameters which can be found from experimental data given in Tables 1–3 for polynitro arenes and polynitro heteroarenes. Multiple linear regression method [30] was used to find adjustable

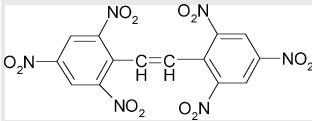
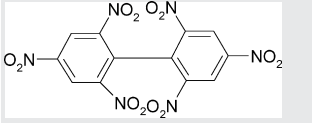
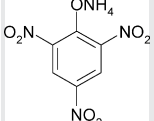
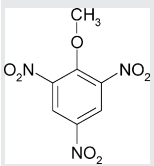
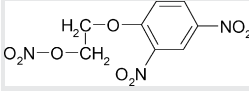
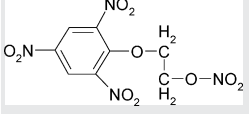
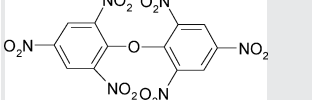
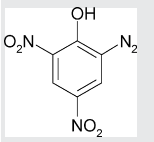
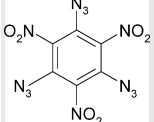
parameters. The left-division method for solving linear equations uses the least squares method because the equation set is overdetermined [30]. The results give the following optimized correlation:

$$\rho = -1.609 + 29.20a' + 1.515b' + 53.06c' + 61.30d' + 0.0703C_{PG} - 0.751C_{NG} \quad (5)$$

The values of C_{PG} and C_{NG} can be specified according to the following situations:

Table 2

Density estimation for some polynitro arenes by new method, previous work [7] and Ammon's method [12].

Explosive	Measured density (g/cm ³)	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Ammon's method	%Error
	1.70 [12]	1.662	2.226	1.674	3.794	1.736	-2.118
	1.60 [31]	1.605	-0.326	1.670	4.393	1.803	-12.688
	1.72 [31]	1.748	-1.607	1.687	1.923	1.721	-0.058
	1.61 [31]	1.610	0.030	1.611	0.081	1.677	-4.161
	1.60 [31]	1.590	0.611	1.589	0.689	1.617	-1.062
	1.68 [31]	1.675	0.322	1.688	0.473	1.712	-1.905
	1.70 [31]	1.680	1.183	1.671	1.713	1.797	-5.706
	1.63 [31]	1.635	-0.319	1.630	0.018	1.734	-6.380
	1.805 [31]	1.827	-1.242	1.805	0.004	1.630	9.695
rms deviation			1.114		2.135		6.279

3.1. Prediction of C_{PG}

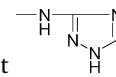
(a) For the presence of $n_{OH} \geq 1$ or $n_{NH_x} \geq 2$ in polynitro arenes as well as in heteroarenes without nitro substituents attached only to polynitro arenes, there is an increase in crystal density of explosive. However, this condition can be applied for polynitro arenes that contain only $-OH$ or $-NH_x$ substituents without extra further substituents such as methyl group. However, $C_{PG} = 1.0$ if $n_{NO_2} - n_{OH} = 1$ (e.g. 3,5-dinitrophenol) or $n_{NO_2} - n_{NH_x} \geq 1$ (e.g. 1,3-diamino-2,4,6-trinitrobenzene); $C_{PG} = 2.0$ if $n_{NO_2} - n_{NH_x} = 0$ (e.g. 1,3,5-triamino-2,4,6-trinitrobenzene); $C_{PG} = 0.5$ if $n_{NO_2} - n_{OH} > 1$ (e.g. picric acid).

(b) $C_{PG} = 1.0$ for polynitro benzene that contain center of symmetry (e.g. p-dinitrobenzene), polynitro heteroarenes with substituent $N-O$ in cycle (e.g. trinitropyridine-N-oxide) and



the explosive containing more than two groups (e.g. benzotris(1,2,5-oxadiazole-1-oxide)).

(c) $C_{PG} = 2.0$ for the explosives that contain positive and negative charges on nitrogens (e.g. tetranitrodibenzo-1,3a,4,6a-tetraazanaphthalene).



(d) $C_{PG} = 3.0$ for polynitro arenes with attachment 3-picrylamino-1,2,4-triazol.

Table 3
Density estimation for some polynitro heteroarenes by new method, previous work [8] and Ammon's method [13].

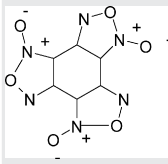
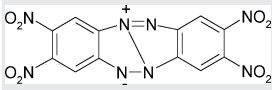
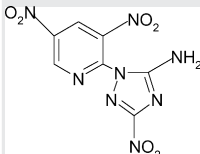
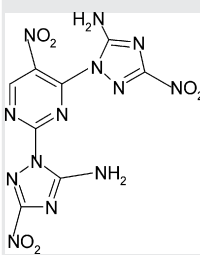
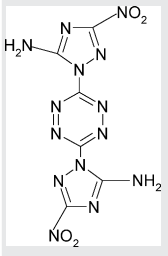
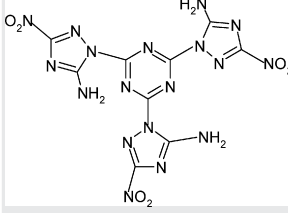
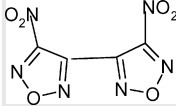
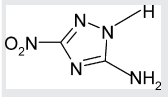
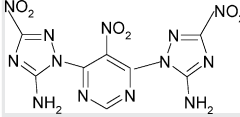
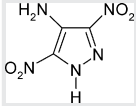
Explosive	Measured density (g/cm ³)	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Ammon's method	%Error
	1.87 [12]	1.880	-0.525	1.813	3.048	1.769	5.401
	1.85 [31]	1.809	2.237	1.850	0.000	1.761	4.811
	1.815 [10]	1.779	1.981	1.736	4.353	1.766	2.700
	1.865 [10]	1.818	2.508	1.777	4.718	1.786	4.236
	1.78 [10]	1.796	-0.921	1.833	-2.978	1.801	-1.180
	1.767 [10]	1.768	-0.069	1.804	-2.094	1.795	-1.585
	1.92 [9]	1.913	0.354	1.872	2.500	1.969	-2.552
	1.819 [10]	1.811	0.425	1.890	-3.903	1.745	4.068
	1.865 [10]	1.818	2.508	1.777	4.718	1.882	-0.912
	1.90 [10]	1.875	1.318	1.877	1.211	1.816	4.421

Table 3 (Continued)

Explosive	Measured density (g/cm ³)	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Ammon's method	%Error
	1.876 [10]	1.798	-1.599	1.803	-1.864	1.831	-3.446
	1.88 [10]	1.906	-1.406	1.880	0.000	1.821	3.138
	1.84 [10]	1.824	0.895	1.856	-0.870	1.752	4.783
	1.918 [10]	1.923	-0.282	1.889	1.512	1.819	5.162
	1.94 [9]	1.926	0.739	1.725	11.082	1.728	10.928
	1.876 [10]	1.853	1.236	1.872	0.213	1.741	7.196
rms deviation			1.418		3.860		4.791

3.2. Prediction of C_{NG}

- The presence of nitrate group can decrease density so that $C_{NG} = 1.0$ for $n_{NO_3} = 1$ and $C_{NG} = 2.0$ for $n_{NO_3} \geq 2$.
- $C_{NG} = 1.0$ for polynitroaromatics with $-N_3$ or $-N_2$ substituents (e.g. diazodinitrophenol) or polynitro arenes containing more than two alkyl substituents (e.g. 1,3,5-trimethyl-2,4,6-trinitrobenzene).
- C_{NG} are 1.5, 1.0 and 0.75 for direct attachment of a polynitro arene cycle (with only nitro substituents) to another polynitro arene cycle (e.g. 2,4,6,2',4',6'-hexanitrobiphenyl), $-OR$ (e.g. trinitroanisole) and $-OAr$ or $-NHAr$ (e.g. 2,4,6,2',4',6'-hexanitrodiphenyl oxide), respectively, where R and Ar are alkyl and aromatic groups.
- $C_{NG} = 1.0$ for polynitro heteroarenes containing amino groups in which more than two heteroatoms exist per each cycle (e.g. 5-amino-3-nitro-1,2,4-triazole).

The constants C_{PG} and C_{NG} are assigned to be zero if the conditions for giving them various values are not met. To demonstrate the present method and test the validity of the correlation, densities of 21 well-known polynitro arenes were calculated and compared with Tarver's method [7] as well as previous work [8]. The predicted results are given in Table 1. Moreover, calculated densities for some further polynitro arenes, where Tarver's method [7] cannot be used, are given Table 2. In Table 2, Ammon's method [13] was used for comparison with the predicted results of new method.

The calculated results for polynitro heteroarenes are also given in Table 3 and compared with previous work [8] and Ammon's method [13]. R-squared values or the coefficients of determination of Eq. (5) is 0.94 [30]. The percent of error in densities, [(predicted-measured)/measured] \times 100, are also given in Tables 1–3. As seen in Tables 1–3, the results of new method are more reliable than Tarver's and Ammon's methods [7,13] as well as previous work [8].

To check the reliability of new method, the calculated values for some further polynitro arenes and polynitro heteroarenes with complex molecular structures are given in Table 4. As seen in Table 4, the same as before, the rms deviation of the new method is less than Ammon's method [13] and previous work [8]. Based on the average density 1.708 g/cm³ in Table 1, the average errors are 0.946, 1.523 and 1.279% for new approach, previous work [8] and Tarver's method [7], respectively. The second series of polynitro arenes, which are listed in Table 2, consist of nine mainly conventional explosives where Tarver's method [7] cannot be applied. Since Tarver's group additivity method [7] cannot be applied for polynitro arenes and polynitro heteroarenes given in Tables 2–4, the new method of Ammon's group additivity [13] was used. The average errors of explosives given in Table 2 are 0.874, 1.454 and 4.864% for new approach, previous work [8] and Ammon's method [13], respectively. The same situations exist for the average errors or the rms deviations in Tables 3 and 4. By considering the greater densities and geometrical complexities of some polynitro arenes and polynitro heteroarenes, the overall agreement of the new approach with reported densities is quite good.

Table 4
Density estimation for some polynitro arenes and polynitro heteroarenes by new method, previous work [7] and Ammon's method [12].

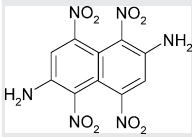
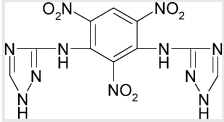
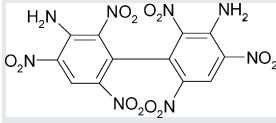
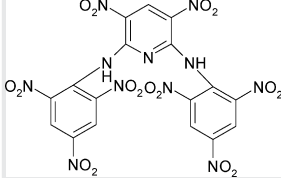
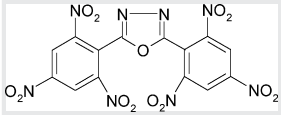
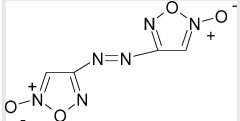
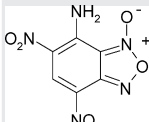
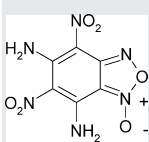
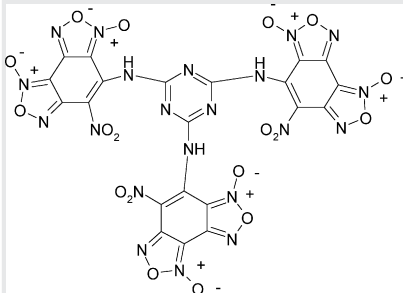
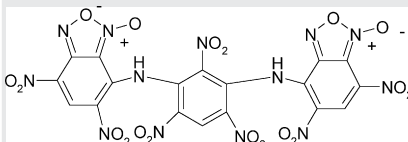
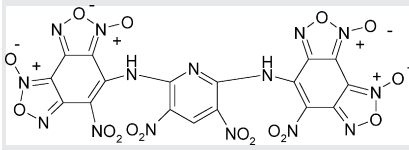
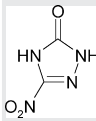
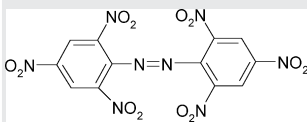
Explosive	Measured density (g/cm ³)	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Ammon's method	%Error
	1.78 [8]	1.745	1.951	1.687	5.216	1.743	2.700
	1.96 [8]	1.929	1.596	1.729	11.775	1.718	4.236
	1.79 [8]	1.809	-1.049	1.693	5.447	1.794	-1.180
	1.75 [8]	1.710	2.287	1.719	1.751	1.799	-1.585
	1.77 [8]	1.717	2.990	1.670	5.669	1.804	-2.552
	2.02 [11]	2.044	-1.188	1.919	5.014	1.828	-0.912
	1.90 [11]	1.835	3.447	1.866	1.770	1.732	0.107
	1.91 [11]	1.850	3.137	1.870	2.070	1.823	0.705
	1.90 [11]	1.849	2.669	1.870	1.580	1.951	4.783
	1.92 [11]	1.828	4.773	1.865	2.885	1.877	4.421

Table 4 (Continued)

Explosive	Measured density (g/cm ³)	Calculated density (g/cm ³) by new method	%Error	Calculated density (g/cm ³) by previous work	%Error	Calculated density (g/cm ³) by Ammon's method	%Error
	1.91 [8]	1.846	3.349	1.869	2.142	1.938	-3.446
	1.91 [11]	1.911	-0.065	1.911	-0.070	1.820	3.138
	1.77 [11]	1.817	-2.649	1.754	0.924	1.768	7.029
rms deviation			2.673		4.637		5.507

4. Conclusions

A new procedure has been developed for simple and reliable prediction of density of polynitro arenes and polynitro heteroarenes. The number of carbons, hydrogens, nitrogens and oxygens as well as the positive and the negative contributions of some specific molecular structure parameters are only important factors that would be needed in the novel method. Quantum mechanical computations, such as *ab initio* method, have a stronger theoretical basis for predictions of density than proposed here but those computations are complex and also require special software. The methodology presented here has the advantage that it gives the simplest and easiest method and at the same time gives reliable results. Comparison of calculated results with experimental data and the outputs of previous work [8] as well as Tarver's and Ammon's group additivity methods [7,13] may be taken as appropriate validation of the new procedure. As compared to Tarver's and Ammon's group additivity estimation methods [7,13], the new procedure exhibits an improved accuracy and simple applicability for two important classes of energetic materials, namely polynitro arenes and polynitro heteroarenes.

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