A reliable simple method to estimate density of nitroaliphatics, nitrate esters and nitramines

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ABSTRACT

In this work, a new simple method is presented to estimate crystal density of three important classes of explosives including nitroalphatics, nitrate esters and nitramines. This method allows reliable prediction of detonation performance for the above compounds. It uses a new general correlation containing important explosive parameters such as the number of carbon, hydrogen, nitrogen and two other structural parameters. The predicted results are compared to the results of best available methods for different family of energetic compounds. This method is also tested for various explosives with complex molecular structures. It is shown that the predicted results are more reliable with respect to the best well-developed simple methods.

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1. Introduction

An accurate prediction of detonation performance and sensitivity is important in selection of a novel energetic compound. Therefore, a chemist must try to synthesize new molecules that yield more energy while difficult to initiate the detonation simultaneously. The Chapman–Jouguet (C–J) pressure, P_{CJ}, is the main detonation parameter in which determines the impulse delivered by an explosive. Experimental data of P_{CJ} for various explosives have shown that this parameter is indeed proportional to the square of the initial density [1]. Thus, to predict a proper detonation performance of an explosive, it would be necessary to have a reliable estimation of density. The C–J pressure of CHNO explosives is predicted by a thermodynamic equilibrium code, such as CHEETAH [2], or various empirical methods [3,4] accurate to within experimental results. It was shown the performance of an explosive is greatly sensitive to its crystalline density, but somewhat less sensitive to its heat of formation [5].

It is not always possible to find experimental values of density or detonation performance for energetic compounds of interest in literature. Since it is not practical to measure density of new energetic compounds, different procedures such as group-contribution and quantum mechanical methods are generally employed. Although there are questions on the accuracy of these methods to predict

reliable estimation of density for nitroaliphatics, nitrate esters and nitramines, recently some correlations have been used to predict density of mentioned compounds [6]. The predicted results by these correlations for some well-known nitrate esters, nitroaliphatics and nitramines are relatively in a good agreement with Traver's method [6,7]. In this work, a new simple method will be introduced that can allow more accurate and reliable prediction of density for nitroaliphatics, nitrate esters and nitramines including large complex compounds. The important structural parameters of explosive such as the molecular weight, the number of carbon, hydrogen and oxygen as well as two other specific molecular structures would control the estimated density. The predicted results are also compared against experimental results of Tarver's method [7], Ammon's group additivity method [8] and previous work [6].

2. Theory

In literature, different methods have been presented to estimate the density of energetic compounds. One approach has been to develop and solve the crystal structure of molecules in 3-dimensional array [9,10]. This approach has some limitations because it must be used by experts and takes much computational efforts.

Another approach using molecular volumes has been used by other scientists to predict the densities of energetic molecules [11]. This method cannot provide accurate density values because it does not consider the void between molecules accurately.

To develop energetic compounds, the *ab initio* crystal structure prediction is a useful molecular simulation technique. It uses a good

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quality model to describe intermolecular interactions among the atoms in crystals. In this technique, the Gaussian 98 program [12] with suitable basis set can be used to perform quantum mechanical calculations. Two examples of recent published results are given here. Rice and Sorescu [13] used a generalized $C_aH_bN_cO_d$ inter-molecular interaction potential marked as the SRT mode in their evaluation. Kim et al. [14] have also calculated the densities of solid energetic molecules with molecular surface electrostatic potential. One must notice that quantum mechanical calculations require high-speed computer to conduct complicated calculations.

The group additivity method is a simple procedure to esti-mate the density of energetic materials. This method is based on summing-up the volume of each atom or molecular fragments. Exner [15] was the first to consolidate the idea of additivity of constituent volumes to estimate the densities for most liquid explo-sives within a standard deviation of 0.008 g/cm^3. Nielsen [16] who extended Exner's method included constituent volumes related to multi-numbered ring systems and chemical entities found in explosives. He found negative and positive contributions to the molar volume for 10–18-member rings and all other ring sys-tems, respectively. Immirzi and Perini [17] defined a set of 15 constituent volumes that are basically atomic volumes. They used a 500 structure database and restricted cyclic compounds to those materials containing benzene and naphthalene rings. Tarver [7] used a database of 188 explosives and related compounds for calcu-lation of densities. Kitiagorodsky [18] has also used the volume of each atom to estimate the molecular volume through an empirically determined van der Waal's radius. Stine [19] comprised 34 param-eters representing specific types of atoms based on the statistics of more than 2000 crystals. Some further works assuming volume additivity have been reported, which are based on single element volumes [20] or molecular salts and hydrates [21]. Ammon and Mitchell [22] developed 78 different groups and atoms from more than 11,000 crystals. Ammon [23] has also expanded the previous work parameters [22] to 96 by examining 26,000 crystals. Finally, Ammon [8] has recently completed his works by introducing an updated atom/functional group and atom_code volume additivity parameters for the calculations of crystal densities.

Different approachhes from mentioned methods have also been introduced to predict densities of energetic compounds. Cho et al. [5] introduced an approach to density prediction based on a holographic quantitative structure–activity relationship. They have shown a large deviation in predicted results from group addi-tivity methods for some energetic materials. It was found that densities for nitroaliphatics, nitrate esters and nitramines can be obtained through some core correlations, which can be corrected in some specific cases [6,24]. For acyclic and cyclic nitrate esters and nitroaliphatics, the core correlation for density was found to be [4]:

$$\rho_0 = \frac{47.972a - 19.295b + 26.534c + 26.001d - 25.319n_{COO} - 0.636n_O + 11.541n_{OH}}{MW} \tag{1}$$

where a, b, c and d are the number of carbon, hydrogen, nitrogen and oxygen atoms, respectively; n_{COO}, n_O and n_{OH} are the number of ester, ether and alcohol functional groups; MW is the molecular weight of explosive and ρ_0 is the core crystal density of explo-sive that should be corrected for some specific cases. For cyclic and acyclic nitramines, the core correlations have been given as followings, respectively [6]:

$$\rho_0 = \frac{13.147a - 5.303b + 39.724c + 29.3395d}{MW} \tag{2}$$

$$\rho_0 = \frac{66.857a - 27.372b + 52.960c + 12.807d}{MW} \tag{3}$$

Although the above method is simple to use, the predicted results for some well-known nitrate esters and nitroaliphatics, where

Tarver's method can be used, show that the reliability of this method is less than Traver's method [7]. Besides, Eq. (2) can be used only for polycyclic nitramines that contain no more than one oxygen in their cyclic structures.

3. Results and discussion

The C–J pressure can be related to detonation velocity through the following equation:

$$P_{CJ} = \frac{\rho'_0 D^2}{\gamma + 1} \tag{4}$$

where P_{CJ} is the C–J pressure, ρ'_0 is the loading density of explosive, D is the detonation velocity and γ is the adiabatic expansion coeffi-cient of the chemical reaction product gases at the C–J state. Eq. (4) implies that P_{CJ} is proportional to the loading density squared [1]. It can be shown through computer codes or empirical methods that a change of 0.1 g/cm^3 on ρ'_0, significantly impacts on the explosive performance, while a difference of 10 kcal/mol in heat of formation had little influence [14].

The study of molecular structures of various nitroaliphatics, nitrate esters and nitramines has shown that it is possible to develop a reliable general correlation for predicting densities of mentioned energetic compounds. It was found that suitable combination of the number of carbon, hydrogen, nitrogen and the molecular weight of explosive as well as two specific structural parameters is important factors for prediction of density which can be given as follows:

$$\rho = z_1 + z_2\frac{a}{MW} + z_3\frac{b}{MW} + z_4\frac{c}{MW} + z_5E_I + z_6E_D \tag{5}$$

where ρ is the crystal density of energetic compound, E_I and E_D are specific structural parameters that can increase or decrease the value of crystal density, z_1–z_6 are adjustable parameters which can be found from experimental data given in Table 1. It should be men-tioned that the number of oxygen has insignificant contribution in this new model because its existence does not change the coeffi-cient of determination of Eq. (5). Multiple linear regression method [25] has been used to find adjustable parameters. Since the equation set is overdetermined, the left-division method for solving linear equations uses the least squares method [25]. The results give the following optimized correlation:

$$\rho = 1.521 + 6.946\frac{a}{MW} - 11.53\frac{b}{MW} + 20.10\frac{c}{MW} - 0.1559E_D$$
$$+ 0.1325E_I \tag{6}$$

R^2 values or the coefficient of determination of Eq. (6) is 0.945 [25]. The values of E_D and E_I can be specified based on molecular structures as:

(a) Nitroaliphatics and nitrate esters
   (1) $C(H)_{4-n}(NO_2 \text{ or } ONO_2)_n$: For nitro or nitrate derivatives of methane, $E_D = 1.70$ and $E_I = 0.0$.
   (2) $C_nH_{2n+1}(NO_2 \text{ or } ONO_2)$: For mononitro- or mononitrate-alkanes, the values of E_D and E_I depend on the number of carbon in alkyl substituents: (i) if $n = 2$, then $E_D = 1$ and $E_I = 0$; (ii) if $n = 3$, then $E_D = 0.5$ and $E_I = 0$; (iii) if $n = 4$, then $E_D = 0$ and $E_I = 0$; (iv) if $n = 5$, then $E_D = 0$ and $E_I = 0.5$; (v) if $n \geq 6$, then $E_D = 0$ and $E_I = 0.75$.
   (3) $C_nH_{2n}(NO_2 \text{ or } ONO_2)_2$: For dinitro- or dinitrate-alkanes, the values of E_D depend on position of attachment of nitro or nitrate groups: (i) for attaching two nitro or nitrate groups to

Table 1
Density estimation for 72 nitroaliphatics, nitrate esters and nitramines by new method, previous work [6] and group additivity methods [7,8].

Energetic compound	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 group additivity methods[a]	%Error
CH_3NO_2	1.1385 [28]	1.132	0.529	1.089	4.382	1.523	−33.773
$CH_3CH_2NO_2$	1.045 [7]	1.050	−0.468	1.038	0.676	1.024	2.010
$CH_3(CH_2)_2NO_2$	1.008 [7]	0.996	1.147	1.003	0.476	1.001	0.694
$CH_3(CH_2)_3NO_2$	0.971 [7]	0.979	−0.793	0.978	−0.711	0.985	−1.462
$CH_3(CH_2)_5NO_2$	0.949 [7]	0.948	0.098	0.944	0.576	0.964	−1.602
$CH_3CH(NO_2)CH_2CH_3$	0.985 [7]	0.979	0.639	0.978	0.721	0.971	1.431
$CH_3CH(NO_2)CH_3$	0.988 [7]	0.996	−0.854	1.003	−1.538	0.984	0.385
$CH_3CH_2CH(NO_2)CH_2CH_3$	0.957 [7]	0.972	−1.585	0.959	−0.174	0.961	−0.418
$CH_3CH(NO_2)_2$	1.35 [7]	1.354	−0.275	1.350	−0.015	1.337	0.963
$CH_3CH_2CH(NO_2)_2$	1.261 [7]	1.227	2.732	1.281	−1.558	1.271	−0.793
$O_2NCH_2C(=0)OCH_2CH_3$	1.1953 [7]	1.196	−0.093	1.218	−1.931	1.188	0.586
$CH_3CH_2ONO_2$	1.10 [7]	1.105	−0.483	1.143	−3.904	1.112	−1.100
$O_2NOCH_2CH_2ONO_2$	1.48 [7]	1.457	1.579	1.499	−1.280	1.485	−0.318
$O_2NOCH_2CH_2CH(ONO_2)CH_2ONO_2$	1.52 [7]	1.552	−2.086	1.537	−1.124	1.521	−0.079
$O_2NOCH_2CH(ONO_2)CH_2CO_2CH(ONO_2)CH_3$	1.47 [7]	1.515	−3.069	1.520	−3.400	1.485	−1.048
$O_2NOCH_2CH_2OCH_2CH_2ONO_2$	1.38 [7]	1.397	−1.260	1.388	−0.551	1.441	−4.420
$O_2NOCH_2CH_2OCH_2OCH_2CH_2ONO_2$	1.33 [7]	1.343	−0.942	1.357	−2.042	1.335	−0.376
$CH_3C(CH_2ONO_2)_3$	1.47 [7]	1.487	−1.147	1.489	−1.326	1.485	−1.048
$(O_2NOCH_2)_3CCH_2OCH_2C(CH_2ONO_2)_2CH_2OCH_2C(CH_2ONO_2)_3$	1.58 [7]	1.505	4.741	1.617	−2.355	1.568	0.766
$O_2NOCH_2CH(ONO_2)CH_2ONO_2$	1.596 [7]	1.625	−1.790	1.591	0.341	1.590	0.363
$O_2NOCH_2(CHONO_2)_4CH_2ONO_2$	1.73 [7]	1.676	3.120	1.729	0.074	1.713	0.994
$(CH_2ONO_2)_4C$	1.77 [7]	1.726	2.484	1.646	6.983	1.765	0.288
$(O_2NOCH_2)_3CCH_2OCH_2OCH_2C(CH_2ONO_2)_3$	1.63 [7]	1.598	1.962	1.625	0.314	1.623	0.460
$(CH_2ONO_2)_3CC(CH_2ONO_2)_3$	1.63 [7]	1.666	−2.216	1.674	−2.709	1.659	−1.779
$O_2NC(CH_2ONO_2)_3$	1.64 [7]	1.657	−1.065	1.637	0.164	1.640	0.000
$O_2NCH_2CH_2NO_2$	1.46 [7]	1.471	−0.729	1.465	−0.364	1.409	3.493
$O_2NCH_2CH_2CH_2NO_2$	1.353 [7]	1.343	0.704	1.382	−2.161	1.329	1.774
$CH_3C(NO_2)_2CH_2CO_2(CH_2)_2CO_2CH_2C(NO_2)_2CH_3$	1.51 [7]	1.491	1.267	1.511	−0.050	1.517	−0.483
$HOCH_2CH_2NO_2$	1.27 [7]	1.314	−3.481	1.270	0.018	1.290	−1.575
$CH_3CH(NO_2)CH_2OH$	1.1841 [7]	1.195	−0.958	1.190	−0.484	1.196	−1.039
$O_2NOCH_2CH(OH)CH_2ONO_2$	1.523 [7]	1.529	−0.419	1.510	0.873	1.549	−1.707
$C_2H_5CH(NO_2)CH_2OH$	1.1332 [7]	1.105	2.522	1.129	0.398	1.151	−1.535
$CH_3C(NO_2)_2CH_3$	1.30 [7]	1.305	−0.346	1.281	1.488	1.312	−0.923
$C(NO_2)_3CH_2CO_2(CH_2)_8CO_2CH_2C(NO_2)_3$	1.45 [7]	1.497	−3.240	1.450	−0.027	1.498	−3.310
$C(NO_2)_3CH_2CO_2(CH_2)_7CO_2CH_2C(NO_2)_3$	1.475 [7]	1.528	−3.570	1.475	0.014	1.526	−3.471
$C(NO_2)_3CH_2CO_2(CH_2)_6CO_2CH_2C(NO_2)_3$	1.59 [7]	1.560	1.883	1.583	0.436	1.557	2.069
$C(NO_2)_3CH_2CO_2(CH_2)_5CO_2CH_2C(NO_2)_3$	1.63 [7]	1.594	2.188	1.609	1.266	1.591	2.387
$HC[OCH_2C(NO_2)_3]_3$	1.8 [7]	1.790	0.546	1.861	−3.405	1.833	−1.856
$H_2C[OCH_2C(NO_2)_3]_2$	1.72 [7]	1.751	−1.827	1.797	−4.455	1.726	−0.366
$C(NO_2)_3(CH_2)_2CO_2(CH_2)_2CO_2(CH_2)_2C(NO_2)_3$	1.63 [7]	1.631	−0.039	1.637	−0.443	1.629	0.074
$C(NO_2)_3CH_2CO_2(CH_2)_4CO_2CH_2C(NO_2)_3$	1.64 [7]	1.631	0.571	1.637	0.169	1.629	0.683
$C(NO_2)_3CH_2CO_2CH_2CO_2CH_2C(NO_2)_3$	1.75 [7]	1.754	−0.213	1.798	−2.728	1.771	−1.217
$C(NO_2)_3(CH_2)_2CO_2CH_2C(NO_2)_3$	1.767 [7]	1.762	0.268	1.736	1.774	1.757	0.589
$C(NO_2)_3CH_2CO_2(CH_2)_3CO_2CH_2C(NO_2)_3$	1.67 [7]	1.669	0.051	1.667	0.193	1.671	−0.054
$(O_2N)_3CC(NO_2)_3$	1.998 [7]	1.969	1.434	1.997	0.029	2.004	−0.300
$C(NO_2)_3(CH_2)_2CO_2CH_2C(NO_2)_2CH_3$	1.68 [7]	1.649	1.854	1.680	−0.006	1.640	2.357
$CH_3C(NO_2)_2CH_2CO_2CH=CHCO_2CH_2C(NO_2)_2CH_3$	1.60 [7]	1.551	3.039	1.620	−1.266	1.553	2.938
$CH_3C(NO_2)_2CH_2CO_2CH=CH_2$	1.47 [7]	1.470	−0.023	1.431	2.657	1.433	2.497
$C_2H_5CO_2(CH_2)_2C(NO_2)_2CH_3$	1.28 [7]	1.296	−1.251	1.309	−2.281	1.278	0.180
$HOCH_2C(CH_2ONO_2)_3$	1.54 [7]	1.542	−0.121	1.540	−0.005	1.570	−1.935
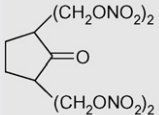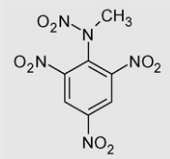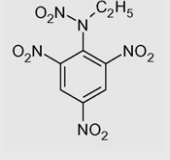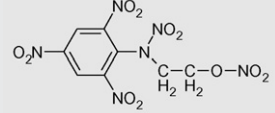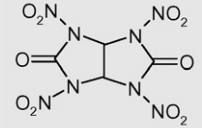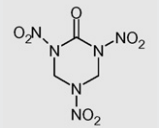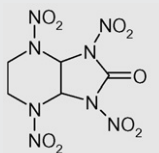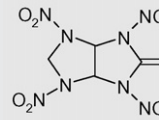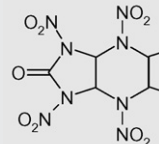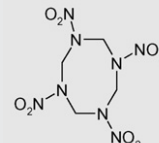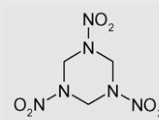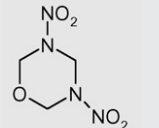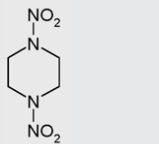
Structure						
(CH₂ONO₂)₂ cyclopentanone di(CH₂ONO₂)₂	1.62 [7]	1.599	1.282	1.678	−3.582	1.620	0.000
nitrocyclopentane	1.0776 [7]	1.096	−1.679	1.099	1.843	1.096	−1.679
nitrocyclohexane	1.061 [7]	1.017	4.147	1.041	−2.000	1.017	4.149
$(CH_3)_2NNO_2$	1.1090 [7]	1.120	−0.969	1.122	−1.209	1.175	−5.951
$(C_2H_5)_2NNO_2$	1.0570 [7]	1.042	1.385	1.061	−0.415	1.050	0.662
$CH_3N(NO_2)(CH_2)_2N(NO_2)CH_3$	1.4460 [7]	1.481	−2.437	1.443	0.238	1.394	3.596
$(C_3H_7)_2NNO_2$	0.9950 [7]	0.976	1.859	1.024	−2.891	1.016	−2.111
$(C_4H_9)_2NNO_2$	0.9620 [7]	0.978	−1.699	0.998	−3.768	0.994	−3.347
$[(CH_3)_2CH]_2NNO_2$	1.1040 [7]	1.076	2.548	1.024	7.268	1.104	0.000
$[(NO_2)_3CCH_2]_2NNO_2$	1.96 [7]	1.988	−1.409	1.961	−0.057	1.932	1.408
N-methyl-trinitroaniline (tetryl)	1.73 [7]	1.762	−1.841	1.738	−0.471	1.739	−0.520
N-ethyl-trinitroaniline	1.63 [7]	1.694	−3.896	1.666	−2.193	1.578	3.190
structure	1.75 [7]	1.739	0.647	1.753	−0.147	1.861	−6.343
structure	2.04 [29]	2.035	0.240	2.028	0.565	2.029	0.539
structure	1.932 [29]	1.925	0.363	1.957	−1.315	1.967	−1.812

Table 1 (*Continued*)

Energetic compound	Measured density (g/cm³)	Calculated density (g/cm³) by new method	%Error	Calculated density (g/cm³) by previous work	%Error	Calculated density (g/cm³) by group additivity methods[a]	%Error
(structure)	1.969 [29]	1.913	2.819	1.912	2.879	1.834	6.856
(structure)	1.91 [29]	1.984	−3.855	1.991	−4.240	1.882	1.466
(structure)	2.05 [29]	2.027	1.124	2.019	1.490	1.918	6.439
(structure)	1.903 [7]	1.847	2.963	1.901	0.110	1.850	2.785
(structure)	1.806 [7]	1.847	−2.249	1.901	−5.255	1.780	1.440
(structure)	1.824 [7]	1.834	−0.534	1.760	3.529	1.824	0.000
(structure)	1.638 [7]	1.612	1.601	1.627	0.649	1.643	−0.305
Rms deviation		1.918		2.258		4.583	

[a] For all compounds, Tarver's method [7] were used except nitromethane in which Ammon's method [8] was used.

Table 2
Density estimation for 41 well-known and new nitramines, nitrate esters and nitroaliphatics by new method and Ammon's method [8].
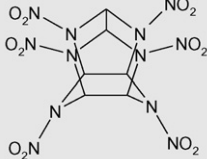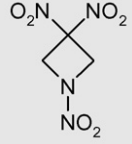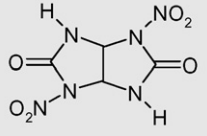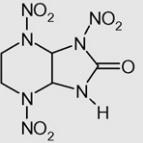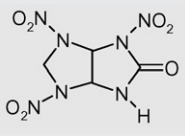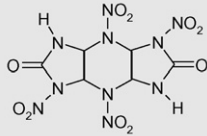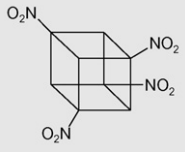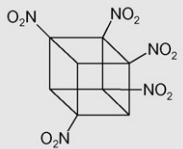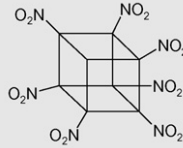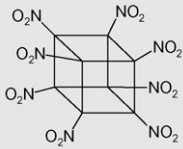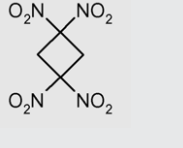
Energetic compound	Measured density (g/cm^3)	Calculated density (g/cm^3) by new method	%Error	Calculated density (g/cm^3) by previous work	%Error	Calculated density (g/cm^3) by Ammon's method	%Error
	2.040 [29]	2.009	1.521	2.000	1.980	2.028	0.588
	1.840 [29]	1.808	1.730	1.839	0.034	1.790	2.717
	1.980 [29]	1.962	0.915	1.921	2.962	1.944	1.818
	1.840 [29]	1.863	−1.254	1.849	0.466	1.845	0.272
	1.905 [29]	1.943	−1.970	1.937	1.697	1.932	1.417
	1.970 [29]	1.980	−0.512	1.952	0.935	1.976	0.305
	1.814 [29]	1.837	−1.292	1.947	7.314	1.816	0.110

Table 2 (*Continued*)
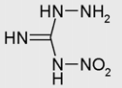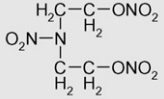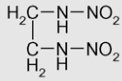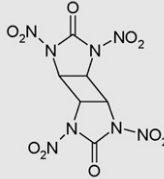
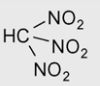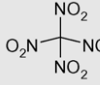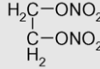| Energetic compound	Measured density (g/cm^3)	Calculated density (g/cm^3) by new method	%Error	Calculated density (g/cm^3) by previous work	%Error	Calculated density (g/cm^3) by Ammon's method	%Error
	1.959 [29]	1.890	3.508	1.945	0.703	1.873	4.390
	2.028 [29]	1.962	3.258	1.943	4.180	1.956	3.550
	1.979 [29]	1.987	−0.421	1.943	1.843	1.987	0.404
	1.830 [29]	1.784	2.510	1.817	0.700	1.908	4.262
CH_3ONO_2	1.217 [28]	1.158	4.837	1.229	0.978	1.648	35.415
	1.590 [28]	1.625	−2.202	1.750	10.078	1.954	22.893
	1.638 [28]	1.702	−3.905	1.848	12.813	2.107	28.656
	1.480 [28]	1.457	1.579	1.499	1.280	1.737	17.365
	1.393 [28]	1.355	2.717	1.429	2.588	1.625	16.655

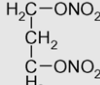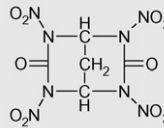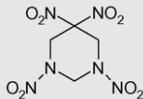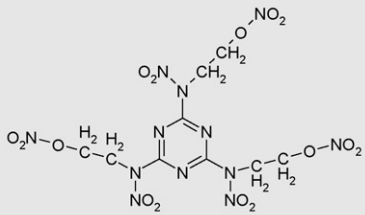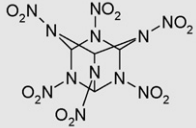| Structure							
H$_2$C—ONO$_2$ / CH$_2$ / O / CH$_2$ / CH$_2$ / O / CH$_2$ / CH$_2$—ONO$_2$	1.335 [28]	1.286	3.684	1.322	0.945	1.450	8.614
H$_3$C—C(H$_2$)—C(H$_2$)—ONO$_2$	1.058 [28]	1.065	−0.614	1.080	2.071	1.350	27.599
H$_3$C—CH(ONO$_2$)—CH$_3$	1.036 [28]	1.065	−2.750	1.080	4.238	1.300	25.483
O$_2$N—C(H$_2$C—ONO$_2$)(C(H$_2$)—ONO$_2$)(H$_2$C—ONO$_2$)	1.680 [28]	1.658	1.341	1.637	2.542	1.788	6.429
O(CH$_2$—CH—CH$_2$—ONO$_2$)	1.332 [28]	1.381	−3.657	1.490	11.884	1.546	16.066
H$_2$C—ONO$_2$ / HC—ONO$_2$ / HC—ONO$_2$ / HC—ONO$_2$ / HC—ONO$_2$ / C(H$_2$)—ONO$_2$	1.604 [28]	1.676	−4.490	1.683	4.923	1.768	10.224
H$_2$C—ONO$_2$ / HC—OH / C(H$_2$)—ONO$_2$	1.510 [28]	1.529	−1.284	1.510	0.020	1.681	11.325
H$_2$C—ONO$_2$ / HC—ONO$_2$ / C(H$_2$)—OH	1.510 [28]	1.529	−1.284	1.510	0.020	1.681	11.325
H$_3$C—C(H$_2$C—ONO$_2$)(C(H$_2$)—ONO$_2$)(H$_2$C—ONO$_2$)	1.460 [28]	1.487	−1.839	1.489	2.020	1.615	10.616

Table 2 (*Continued*)

Energetic compound	Measured density (g/cm³)	Calculated density (g/cm³) by new method	%Error	Calculated density (g/cm³) by previous work	%Error	Calculated density (g/cm³) by Ammon's method	%Error
(structure)	1.412 [28]	1.444	−2.256	1.547	9.577	1.557	10.269
(structure)	1.500 [28]	1.429	4.750	1.447	3.543	1.549	3.267
(structure)	1.600 [28]	1.650	−3.140	1.637	2.291	1.760	10.000
(structure)	1.320 [28]	1.386	−5.030	1.370	3.790	1.320	0.000
(structure)	1.630 [28]	1.532	6.027	1.573	3.499	1.658	1.718
(structure)	1.520 [28]	1.541	−1.361	1.558	2.494	1.643	8.092
(structure)	1.520 [28]	1.552	−2.086	1.537	1.124	1.671	9.934
(structure)	1.710 [28]	1.684	1.536	1.873	9.549	1.680	1.754

Structure							
(structure)	1.710 [28]	1.706	0.245	1.852	8.315	1.665	2.632
(structure)	1.488 [28]	1.510	−1.453	1.511	1.576	1.665	11.895
(structure)	1.710 [28]	1.689	1.253	1.550	9.337	1.635	4.386
(structure)	1.990 [30]	1.970	0.986	1.922	3.417	2.017	1.357
(structure)	1.980 [30]	1.966	0.720	1.952	1.439	2.021	2.071
(structure)	1.820 [30]	1.819	0.062	1.856	2.005	1.893	4.011
(structure)	1.730 [30]	1.756	−1.522	2.085	20.519	1.763	1.908
(structure)	2.100 [30]	2.062	1.809	2.088	0.585	2.114	0.667
Rms deviation			2.605		5.841		12.178

one primary carbon, simultaneously, $E_D = 1.5$; (ii) for attaching two nitro or nitrate groups to one secondary carbon, simultaneously, $E_D = 1.0$; (iii) for the other cases, $E_D = 0.75$. $E_I = 0$ for these compounds.

(4) For the existence of OH in all nitro or nitrate compounds, $E_I = 0.4$ and $E_D = 0.0$.

(5) For some nitrate compounds without OH group, E_I is 1.0 for the presence of $(CH_2ONO_2)_4{}^-$ and $E_I = 0.5$ for compounds that contain $(CH_2ONO_2)_3{}^-$ or two $(CH_2ONO_2)_2{}^-$. $E_D = 0$ for mentioned compounds.

(b) Nitramines

(1) $(C_nH_{2n+1})_2NNO_2$: for these nitramines, the number of carbon is important for prediction of E_D and E_I. (i) If $n = 1$, then $E_D = 1.5$ and $E_I = 0.0$; (ii) if $n = 2$, then $E_D = 0.5$ and $E_I = 0.0$; (iii) if $n = 3$, then $E_D = 0.0$ and $E_I = 0.0$; (iv) if $n \geq 4$, then $E_D = 0.0$ and $E_I = 0.75$.

(2) For some nitramines that have specific molecular structures, E_D and E_I have certain values: (i) for the presence of aromatic ring, $E_D = 0.5$ and $E_I = 0.0$; (ii) for the existence of NH–NO$_2$ functional group, $E_D = 1.5$ and $E_I = 0.0$; (iii) for cyclic ether and the existence of $(NO_2)_3C^-$ group, E_I are 1.0 and 0.5 respectively. The value of E_D is zero for this state.

As seen in Eq. (6), coefficients of E_D and E_I have negative and positive values, respectively, which can provide a suitable pathway for getting higher densities in new explosives. Further, the parameter "n" in each family of mentioned energetic compounds has large effect. Since density of materials in liquid state depends on temperature, it is to be noted that Eq. (6) can predict density of nitroaliphatics, nitrate esters and nitramines near room temperature. For example, densities of nitromethane at 20 and 30 °C are 1.13816 and 1.12439 g/cm^3, respectively [26]. Eq. (6) is not suitable for polynitroaromatic compounds that contain –NO$_2$ only in form Ar–NO$_2$. As an example, the measured density for m-dinitrobenzene is 1.575 g/cm^3 while its predicted density by Eq. (6) is 1.735 g/cm^3. For nitroaromatic energetic compounds, the other useful methods can be used [24,27]. Although, in particular, on the compounds for which in Tables 1 and 2, the error with respect to the experimental value is rather high compare to other energetic compounds in the same family, however, the reliability of present method is higher than previous works [6–8]. It should be noticed that the best optimized values of E_D and E_I were chosen in each family.

To test the credibility of the present method, the results should be compared with results of other techniques. Therefore, Tarver's [7] and Ammon's [8] methods as well as previous work [6] were used for this purpose. Some well-known and new explosives were also given in Table 2 and compared with measured data as well as previous work [6] and Ammon's method [8]. The predicted results of Ammon's method [8] were used in Table 2 because the crystal density for most of these compounds cannot be calculated by Tarver's method [7]. The percent error in densities [(predicted − measured)/measured] × 100, are also given in Tables 1 and 2. As presented in Tables 1 and 2, the reliability of the data for present method is more than the best available simple methods.

4. Conclusions

The density is a primary property of an explosive for prediction of its performance because the Chapman–Jouguet (C–J) pressure is proportional to the square of initial density [4]. A novel and simple method has been introduced to predict the densities of nitroaliphatics, nitrate esters and nitramines. This model is based on the molecular weight, the number of carbon, hydrogen and

nitrogen of explosive as well as the existence of some specific structural parameters that can increase or decrease the value of crystal density. The predicted results for the above compounds, with available required data in open literature, were compared with the experimental data and three acceptable methods. As shown in Tables 1 and 2, new method presents an improved accuracy and applicability compared to the best available simple methods.

Acknowledgement

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