Research paper

A Simple Approach for Predicting the Density of High Nitrogen Organic Compounds as Materials for Providing Clean Products and Enormous Energy Release

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Abstract: High nitrogen organic compounds (N>50 wt.%) are important for chemical industries because they can provide clean products with generally low-molecular weight product gases and enormous energy release. The density of these materials at or near room temperature is an important physical property for the assessment of their detonation and combustion performances. A novel method is introduced here for the prediction of the density of various classes of organic compounds, including different derivatives of triazole, tetrazole, triazine, tetrazine, furazan, and some organic nitrogen-containing chains. The core model is based on elemental composition, where its reliability has been improved by considering some molecular fragments including specific functional groups. The high reliability of these simple model has been compared with the output from two complex quantum mechanical approaches. For 91 high nitrogen compounds, the values of the standard deviation (*SD*) of the core and improved correlations were 0.076 and 0.047 g·cm^{-3}. For a further 32 materials, the values of *SD* were 0.057 and 0.042 g·cm^{-3} for the core and improved correlations, respectively. These data are close to core and improved quantum mechanical methods, *i.e.* 0.056 and 0.042 g·cm^{-3}, respectively, where the calculated data from complex quantum mechanical approaches were available.

Keywords: density, high nitrogen organic compounds, molecular structure, clean product, enormous energy release

List of Important Symbols

a	The number of carbon atoms
b	The number of hydrogen atoms
c	The number of nitrogen atoms
d	The number of oxygen atoms
Mw	Molecular weight of the desired high nitrogen compound
$Mw_{molecule}$	Molecular mass of the molecule
ρ	Density
ρ_{core}	Core density
$\rho^{+}_{non-add}$	Increasing factor for non-additive function of density
$\rho^{-}_{non-add}$	Decreasing factor for non-additive function of density
AD	Average deviation
AD_{max}	Absolute maximum deviation
R^2	Coefficient of determination
SD	Standard deviation of model
sd	Standard deviation of each individual coefficient

1   Introduction

Nitrogen-rich compounds liberate high energy because they usually have high positive heats of formation. Since the presence of N–N and N=N bonds in nitrogen-rich compounds, with the average energies for N–N bonds (160 kJ/mol) and N=N bonds (418 kJ/mol) being much lower than N≡N (954 kJ/mol), nitrogen-rich compounds can provide enormous energy release [1, 2]. For detonation and combustion processes, the main product of nitrogen-rich compounds is N_2 gas [3, 4]. Therefore, they can provide clean products with, generally, low-molecular weight gases [5-7]. Since nitrogen-rich compounds have low numbers of carbon and hydrogen atoms, they have higher densities and good oxygen balance, which are further advantages [8, 9].

The density of an energetic compound is a very important parameter for an assessment of its detonation velocity and pressure [10-13]. Moreover, it is desirable to use nitrogen-rich compounds with high densities as propellants in order to obtain an effective combustion process [14]. Common high detonation performance explosives, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), contain nitrogen contents up to 38 wt%. High nitrogen organic compounds, defined as those with more than 50 wt% nitrogen in their molecular structures [15],

often contain derivatives of triazole, tetrazole, triazine, tetrazine, furazan, and organic nitrogen-containing chains up to 88 wt.% nitrogen in their structures. Most high nitrogen organic materials are derivatives of five or six membered cycles or nitrogen-containing chains, which have a variety of nitrogen-containing fragments such as $-NH_2$, $-NO_2$, $-N_3$, $-C≡N$, $-N=N-$, $-C=N-$ and $-N=N^+O^-$. Due to the importance of high nitrogen organic compounds, they are suitable candidates for insensitive high explosives [1], gun propellants [16-18], and clean gas generators in vehicle airbags [5, 19].

Different methods have been developed for predicting the density of different classes of organic compounds containing energetic functional groups. These include group additivity, quantum mechanics [20-25], quantitative structure-property relationship (QSPR) methods [26, 27], and molecular fragments including some specific functional groups [13]. Quantum mechanical calculations need expensive and intensive computations with specific software, as well as expert operators. Thus, they can only be used for relatively small molecules. In contrast to quantum mechanical methods, group additivity methods are simple to use but they cannot be used for the compounds containing unusual chemical structures and complex molecular structures, because these may give large deviations from experimental data. QSPR models usually require complex molecular descriptors and different computational tools, such as multiple linear regression (MLR), non-linear regression (NLR), partial least squares (PLS), artificial neural networks (ANN), genetic algorithms (GA), and support vector machines (SVM) [13, 28]. For some classes of organic compounds and ionic liquids containing energetic functional groups, it was shown that molecular fragments including some specific functional groups can also be used to predict their densities with good reliability [28-39]. These methods should be used only for specific classes of organic compounds, because they may give large deviations for other classes of organic materials.

The purpose of the present work was to introduce a new approach for predicting the density of high-nitrogen organic compounds, at or near room temperature, containing triazoles, tetrazoles, triazines, tetrazines, furazans, and some organic chains with more than 50 wt.% nitrogen. The core correlation was derived, based on experimental data that have been collected from different sources, by considering their elemental compositions. Its reliability is improved by two correcting factors. To test the reliability of the new correlations, the predicted results for further high nitrogen organic compounds is compared with two complex quantum mechanical methods, where the output for high nitrogen organic compounds was available [22]. It is shown that application of the new correlations for different complex high nitrogen molecules is straightforward

and very simple. Moreover, the new method will provide predictions as good as those reported by complex quantum mechanical approaches.

2   Development of the New Model

Previous studies have confirmed that elemental composition has an important role in predicting the densities of different classes of organic compounds containing energetic functional groups [28-35, 37, 38], as well as ionic liquids [36, 39]. Moreover, some molecular fragments have significant effects on the densities of organic molecules. The study of experimental values of the densities of high nitrogen compounds, at or near room temperature, showed that it is possible to correlate their densities with elemental composition, as well as specific functional groups and molecular fragments, under certain conditions. Table 1 lists the experimental data of densities for 91 high nitrogen compounds, which have been collected from different sources.

These data have been used to construct the new model by the MLR method [83]. It was found that the ratio of elemental composition to molecular weight of organic compounds containing energetic functional groups could improve the correlation coefficient significantly [32-35, 37, 38]. Thus, the core correlation as the additive part for high nitrogen organic materials with the empirical formula of $C_aH_bN_cO_d$ was derived as follows:

$$\rho_{core}= 2.216 – 9.098(a/Mw) – 5.202(b/Mw) – 5.569(c/Mw) \tag{1}$$

where ρ_{core} is the core density in g·cm^{-3}; a, b, c, and d are the numbers of carbon, hydrogen, nitrogen, and oxygen atoms; Mw is the molecular weight of the high nitrogen compound. The coefficient of determination in the MLR method (R^2) [83] measures the proportion of variation in the dependent variable that can be predicted from the set of independent variables. The value of R^2 for Equation 1 was 0.706. Since the presence of the ratio of oxygen atoms (d) to Mw cannot improve the value of R^2, the contribution of d/Mw has been neglected. It was found that the presence of some specific functional groups and molecular fragments leads to large deviations of the predicted results of Equation 1 from experimental data. Table 2 lists these functional groups and molecular fragments. Thus, the reliability of Equation 1 can be improved by considering non-additive correcting functions as:

Table 1. Comparison of the predicted results from Equations 1 and 2 for 91 high nitrogen organic compounds with experimental data (g·cm⁻³)

Name	Composition	Exp.	N wt%	Equation 1	Dev	Equation 2	Dev
3,3'-Bis(4-(5-methyl-1H-1,2,4-triazol-3-yl)-4,4'-azofurazan	$C_{10}H_8N_{12}O_2$	1.81 [40]	51.2	1.608	-0.202	1.817	0.007
Tris[2-(5-amino-1H-tetrazol-1-yl)ethyl]amine	$C_9H_{18}N_{16}$	1.492 [41]	63.98	1.46	-0.032	1.451	-0.041
(Z,Z,Z)-N,N',N''-(1,1',1''-(Nitrilotris(ethane-2,1-diyl))tris(1H-tetrazole-1(4H)-yl-5(4H)-ylidene))trinitramide	$C_9H_{15}N_{19}O_6$	1.616 [42]	54.84	1.668	0.0519	1.669	0.053
(1R,2R)-1,2-Bis(5-amino-1H-tetrazol-1-yl)cyclohexane	$C_8H_{14}N_{10}$	1.453 [41]	55.98	1.411	-0.042	1.401	-0.052
(1R,4R)-1,4-Bis(5-amino-1H-tetrazol-1-yl)cyclohexane	$C_8H_{14}N_{10}$	1.46 [41]	55.98	1.411	-0.049	1.401	-0.059
3,3',5,5'-Tetra(azidomethyl)-4,4'-azo-1,2,4-triazole	$C_8H_8N_{20}$	1.534 [43]	72.9	1.628	0.0938	1.553	0.019
(5-Azido-1H-tetrazol-1-yl)-[6-(5-azido-1H-imino)cyclohexenyl]amine	$C_8H_8N_{16}$	1.65 [44]	68.28	1.595	-0.055	1.573	-0.077
N,N'-Bis(5-azido-1H-tetrazol-1-yl)-1,4-diiminocyclohexane	$C_8H_8N_{16}$	1.63 [44]	68.28	1.595	-0.035	1.573	-0.057
3,3'-Bis(4-amino-1H-1,2,4-triazol-5(4H)-one)-4,4'-azofurazan	$C_8H_6N_{14}O_4$	1.68 [40]	54.13	1.713	0.0331	1.703	0.023
3,3'-Bis[(1H-1,2,4-triazol-5-amine)-diyl]-4,4'-azofurazan	$C_8H_6N_{14}O_2$	1.79 [40]	59.38	1.664	-0.126	1.814	0.024
3,6-Bis(2-(4,6-diazido-1,3,5-triazin-2-yl)-hydrazinyl)-1,2,4,5-tetrazine	$C_8H_4N_{26}$	1.755 [45]	78.43	1.702	-0.053	1.675	-0.080
Di(5-nitramino-1,2,4-triazoly)-azo-furazan	$C_8H_4N_{16}O_6$	1.873 [46]	53.32	1.781	-0.092	1.880	0.007
3,3'-Bis(5-amino-1,2,4-oxadiazol-3-yl)-4,4'-azo-furazan	$C_8H_4N_{12}O_4$	1.85 [40]	50.59	1.733	-0.117	1.840	-0.010
3,3'-Bis (5-amine-1,3,4-oxadiazol-yl)-4,4'-azofurazn	$C_8H_4N_{12}O_4$	1.83 [40]	50.59	1.733	-0.097	1.840	0.010
3,6-bis-(2-(4,6-diazido-1,3,5-triazin-2-yl)-diazenyl)-1,2,4,5-tetrazine	C_8N_{26}	1.763 [45]	79.12	1.743	-0.02	1.711	-0.052
2,5,8-Triazido-s-heptazine	C_6N_{16}	1.823 [47]	75.66	1.73	-0.093	1.698	-0.125
(Z,Z)-N,N'-(1,1'-(Butane-1,4-diyl)bis(1H-tetrazole-1(4H)-yl-5(4H)-ylidene))dinitramide	$C_6H_{10}N_{12}O_4$	1.579 [42]	53.49	1.663	0.0844	1.665	0.086
1,3,5-Tri(1-methyltetrazol-5-yl)pentazadiene	$C_6H_9N_{17}$	1.532 [48]	74.59	1.601	0.0691	1.584	0.052
1,3,5-Tri(2-methyltetrazol-5-yl)pentaza-1,4-diene	$C_6H_9N_{17}$	1.524 [48]	74.59	1.601	0.0771	1.584	0.060
1-(2-(1H-Pyrazol-1-yl)ethyl)-1H-tetrazol-5-amine	$C_6H_9N_7$	1.39 [49]	54.73	1.431	0.0415	1.418	0.028

Name	Composition	Exp.	N wt%	Equation 1	Dev	Equation 2	Dev
(E)-1-1-(2-(1H-Pyrazol-1-yl)ethyl)-5-(hydroxydiazenyl)-1Htetrazole	$C_6H_8N_8O$	1.5 [49]	53.83	1.539	0.0391	1.529	0.029
1-(2-(3,5-Diazido-4-nitro-1H-pyrazol-1-yl)ethyl)-1H-tetrazol-5-amine	$C_6N_{14}O_2$	1.63 [50]	64.04	1.681	0.0506	1.667	0.037
1-(2-(4-Azido-3,5-dinitro-1H-pyrazol-1-yl)ethyl)-1H-tetrazol-5-amine	$C_6H_6N_{12}O_4$	1.7 [50]	54.18	1.723	0.0234	1.719	0.019
Tris(triazolo)benzene	$C_6H_3N_9$	1.77 [51]	62.67	1.617	-0.153	1.778	0.008
1,2-Bis(5-azido-4-nitro-1H-imidazol-1-yl)diazene	$C_6H_2N_{14}O_4$	1.77 [52]	58.67	1.788	0.0177	1.776	0.006
3,3'-Bis(1H-tetrazol-5-yl)-4,4'-azofurazan	$C_6H_2N_{14}O_2$	1.69 [40]	64.89	1.742	0.0524	1.722	0.032
3,3'-Dicyano-4,4'-azofurazan	$C_6N_8O_2$	1.62 [40]	51.84	1.757	0.1368	1.681	0.061
1,4-Bis(azidomethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-c]pyrazole	$C_6H_4N_{12}O_4$	1.71 [53]	54.53	1.754	0.044	1.694	-0.016
4,8-Bis(azidomethyl)-4H,8H-bis([1,2,5]oxadiazolo)[3,4-b:3',4'-e]pyrazine	$C_6H_4N_{12}O_2$	1.68 [53]	60.86	1.7	0.0205	1.684	0.004
1,3-Bis(5-amino-1H-tetrazol-1-yl)propan-2-ol	$C_5H_{10}N_{10}O$	1.585 [41]	61.93	1.538	-0.047	1.533	-0.052
1,3-Bis(5-amino-1H-tetrazol-1-yl)propane	$C_5H_{10}N_{10}$	1.567 [41]	66.65	1.486	-0.081	1.476	-0.091
1,2-Bis(4,5-dihydro-5-nitroimino-1H-tetrazol-1-yl)propane	$C_5H_8N_{12}O_4$	1.658 [42]	55.99	1.703	0.0447	1.704	0.046
1-[1,3-Diazido-2-(azidomethyl)-2-propyl]-3-nitrourea	$C_5H_8N_{12}O_3$	1.54 [54]	59.14	1.674	0.1337	1.535	-0.005
1-(2-(5-Amino-3-nitro-1H-1,2,4-triazol-1-yl)ethyl)-1H-tetrazol-5-amine	$C_5H_8N_{10}O_2$	1.66 [50]	58.32	1.621	-0.039	1.616	-0.044
1,3-Bis((Z)-5-(nitroimino)-4,5-dihydro-1H-tetrazol-1-yl)propan-2-yl nitrate	$C_5H_7N_{13}O_7$	1.759 [42]	50.41	1.788	0.0293	1.795	0.036
1-(2-(3-Nitro-1H-1,2,4-triazol-1-yl)ethyl)-1H-tetrazol-5-amine	$C_5H_7N_9O_2$	1.58 [50]	55.99	1.629	0.049	1.623	0.043
(Z)-N-(1-(2-(3-nitro-5-(nitroamino)-1H-1,2,4-triazol-1-yl)ethyl)-1,4-dihydro-5H-tetrazol-5-ylidene)nitramide	$C_5H_6N_{12}O_6$	1.8 [50]	50.9	1.781	-0.019	1.785	-0.015
(Z)-N-(1-(2-(3-nitro-1H-1,2,4-triazol-1-yl)ethyl)-1H-tetrazol-5(4H)-ylidene)nitramide	$C_5H_6N_{10}O_4$	1.69 [50]	51.84	1.725	0.0354	1.725	0.035

Name	Composition	Exp.	N wt%	Equation 1	Dev	Equation 2	Dev
1,2-Bis(5-amino-1H-tetrazol-1-yl)ethane	$C_4H_8N_{10}$	1.567 [41]	71.41	1.534	−0.033	1.522	−0.045
4,4′,5,5′-Tetraamino-3,3′-bi-1,2,4-triazole	$C_4H_8N_{10}$	1.68 [55]	71.41	1.534	−0.146	1.688	0.008
1,1′-Ethylenebis(oxy)bis(5-nitroiminotetrazole)	$C_4N_{12}O_6$	1.81 [56]	52.82	1.793	−0.017	1.799	−0.011
1,2-Bis(4,5-dihydro-5-nitroimino-1H-tetrazol-1-yl)ethane	$C_4H_6N_{12}O_4$	1.858 [42]	58.73	1.746	−0.112	1.746	−0.112
5,5′-Diamino-4,4′-dinitramino-3,3′-bi-1,2,4-triazole	$C_4H_6N_{12}O_4$	1.756 [57]	58.73	1.746	−0.01	1.746	−0.010
N,N^2-Bis(5-amino-1H-tetrazol-1-yl)oxalamide	$C_4H_6N_{12}O_2$	1.65 [58]	66.13	1.687	0.0365	1.679	0.029
1-(2-(5-Nitro-2H-tetrazol-2-yl)ethyl)-1H-tetrazol-5-amine	$C_4H_6N_{10}O_2$	1.7 [50]	61.94	1.67	−0.03	1.664	−0.036
3,3′-Diamino-4,4′-azo-1,2,4-triazole	$C_4H_6N_{10}$	1.61 [59]	72.15	1.58	−0.03	1.563	−0.047
4-Amino-3,5-di(azidomethyl)-1,2,4-triazole	$C_4H_6N_{10}$	1.563 [43]	72.15	1.58	0.0172	1.563	0.000
3-amino-4-(5-amino-1,2,4-triazol-3-yl)furazan	$C_4H_5N_7O$	1.596 [60]	58.67	1.609	0.0127	1.598	0.002
2,2′-(Oxybis(methylene))bis(5-nitro-1H-tetrazole)	$C_4H_4N_{10}O_5$	1.846 [61]	51.46	1.801	−0.045	1.803	−0.043
3,3′-Diamino-5,5′-dinitro-4,4′-bis(1,2,3-triazole)	$C_4H_4N_{10}O_4$	1.85 [62]	54.68	1.775	−0.075	1.774	−0.076
5,5′-Dinitro-2H,2′H-3,3′-bi(1,2,4-triazole)-2,2′-diamine	$C_4H_4N_{10}O_4$	1.83 [63]	54.68	1.775	−0.055	1.774	−0.056
2,3′-Diamino-5,5′-dinitro-4,4′-bis(1,2,3-triazole)	$C_4H_4N_{10}O_4$	1.84 [62]	54.68	1.775	−0.065	1.774	−0.066
2,2′-Diamino-5,5′-dinitro-4,4′-bis(1,2,3-triazole)	$C_4H_4N_{10}O_4$	1.85 [62]	54.68	1.775	−0.075	1.774	−0.076
3,3′-Diamino-4,4′-azoxyfurazan (DAAF)	$C_4H_4N_8O_3$	1.745 [3]	52.82	1.736	−0.009	1.733	−0.012
5-(5-Amino-1H-1,2,4-triazol-3-yl)-3-nitro-1H-1,2,4-triazole	$C_4H_4N_8O_2$	1.61 [64]	57.13	1.697	0.0866	1.688	0.078
5-(5-Nitrimino-1,3H-1,2,4-triazol-3-yl)-3-nitro-1H-1,2,4-triazole	$C_4H_3N_9O_4$	1.7 [64]	52.27	1.792	0.092	1.790	0.090
1,2-Bis(3-nitro-1H-1,2,4-triazol-1-yl)diazene	$C_4H_2N_{10}O_4$	1.8 [52]	55.11	1.812	0.0123	1.807	0.007
5-(5-Azido-1H-1,2,4-triazol-3-yl)-3-nitro-1H-1,2,4-triazole	$C_4H_2N_{10}O_2$	1.68 [64]	63.05	1.754	0.0741	1.739	0.059
Urea 2-methyl-5-nitraminotetrazole	$C_3H_8N_8O_3$	1.56172 [65]	54.89	1.66	0.0979	1.670	0.108
1,3-Bis(5-amino-1H-tetrazol-1-yl)urea	$C_3H_6N_{12}O$	1.65 [58]	74.33	1.661	0.0112	1.651	0.001
3,4,5-Triamino-1-tetrazolyl-1,2,4-triazole (TATT)	$C_3H_6N_{10}$	1.685 [66]	76.91	1.588	−0.097	1.693	0.008
3,6,7-Triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazole	$C_3H_6N_8$	1.725 [67]	72.71	1.547	−0.178	1.701	−0.024
1-(2-Azidoethyl)-5-aminotetrazole polymorph II	$C_3H_6N_8$	1.4763 [68]	72.71	1.547	0.0703	1.534	0.058
1-Methyl-5-(methylnitramino)-1H-tetrazole	$C_3H_6N_6O_2$	1.522 [47]	53.15	1.634	0.112	1.513	−0.009
1-(2-Azidoethyl)-5-nitriminotetrazole	$C_3H_5N_9O_2$	1.64088 [68]	63.31	1.696	0.0552	1.692	0.051

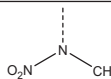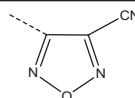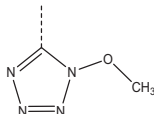| Name	Composition	Exp.	N wt%	Equation 1	Dev	Equation 2	Dev
1,1'-Methylenebis(oxy)bis(5-nitroiminotetrazole)	$C_2H_4N_{12}O_6$	1.9 [56]	55.26	1.838	−0.062	1.844	−0.056
5,5'-(Hydrazonomethylene)bis(1H-tetrazole)	$C_3H_4N_{10}$	1.71 [69]	77.76	1.639	−0.071	1.620	−0.090
5-(5-Nitrimino-1,4H-1,2,4-triazol-3-yl)tetrazol-1-ol	$C_3H_3N_9O_3$	1.85 [70]	59.15	1.779	−0.071	1.776	−0.074
5-(5-Nitrimino-1,2,4-triazol-3-yl)-tetrazole	$C_3H_3N_9O_2$	1.7 [70]	63.95	1.744	0.0436	1.735	0.035
3-Nitro-1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine	$C_3H_3N_9O_2$	1.77 [71]	63.95	1.744	−0.026	1.735	−0.035
Di(1H-tetrazol-5-yl)methanone oxime	$C_3H_3N_9O$	1.74 [69]	69.6	1.702	−0.038	1.687	−0.053
5-Azido-4-nitro-1H-imidazol-1-amine	$C_3H_3N_7O_2$	1.65 [72]	57.98	1.731	0.0812	1.725	0.075
5-Azido-3,4-dinitro-1H-pyrazol-1-amine	$C_3H_2N_8O_4$	1.82 [73]	52.33	1.831	0.0114	1.832	0.012
5-(3-Nitro-1H-1,2,4-triazol-5-yl)tetrazol-1-ol	$C_3H_2N_8O_3$	1.86 [70]	56.56	1.8	−0.06	1.796	−0.064
5-(5-Nitro-1,2,4-triazol-3-yl)-tetrazole	$C_3H_2N_8O_2$	1.7 [70]	61.53	1.764	0.0638	1.754	0.054
5-Nitrotetrazol-2-ylacetonitrile	$C_3H_2N_6O_2$	1.72169 [74]	54.53	1.754	0.0323	1.746	0.024
5-Amino-1-methoxy-1H-tetrazole	$C_2H_5N_5O$	1.503 [41]	60.86	1.589	0.0862	1.487	−0.016
5,5'-Hydrazinebistetrazole (HBT)	$C_2H_4N_{10}$	1.86195 [75]	83.32	1.652	−0.21	1.826	−0.036
1-Methoxy-5-nitroiminotetrazole	$C_2H_4N_6O_3$	1.66 [56]	52.49	1.763	0.1032	1.668	0.008
3-Nitro-1H-1,2,4-triazole-1,5-diamine	$C_2H_4N_6O_2$	1.76 [73]	58.33	1.713	−0.047	1.716	−0.044
2,4-Diamino-5-nitro-1,2,3-triazole	$C_2H_4N_6O_2$	1.73 [76]	58.33	1.713	−0.017	1.716	−0.014
3,4-Diamino-5-nitro-1,2,3-triazole	$C_2H_4N_6O_2$	1.71 [76]	58.33	1.713	0.0029	1.716	0.006
5,5'-Bis(1H-tetrazolyl)amine	$C_2H_3N_9$	1.83404 [77]	82.34	1.667	−0.167	1.838	0.004
3-Nitro-1H-1,2,4-triazol-1-amine	$C_2H_3N_5O_2$	1.68 [73]	54.26	1.738	0.0579	1.741	0.061
1-Nitroamino-1,2,3-triazole	$C_2H_3N_5O_2$	1.8 [78]	54.26	1.738	−0.062	1.812	0.012
4-Nitroamino-1,2,4-triazole	$C_2H_3N_5O_2$	1.82 [78]	54.26	1.738	−0.082	1.812	−0.008
1-(2H-Tetrazol-5-yl)-5-nitraminotetrazole	$C_2H_2N_{10}O_2$	1.77 [79]	70.7	1.79	0.02	1.781	0.011
Nitroaminoguanidine	$CH_5N_5O_2$	1.71 [12]	58.82	1.687	−0.023	1.704	−0.006
1,5-Di(nitramino)tetrazole	$CH_2N_8O_4$	1.93 [80]	58.94	1.879	−0.051	1.887	−0.043
5-Azido-1H-tetrazole	CHN_7	1.67039 [81]	88.28	1.736	0.0653	1.713	0.043
5-Nitro-2-hydroxytetrazole	CHN_5O_3	1.90469 [82]	53.43	1.894	−0.011	1.902	−0.002
1-Methyl-5-(methylnitramino)-1H-tetrazole	$C_3H_6N_6O_2$	1.522 [47]	53.15	1.634	0.112	1.513	−0.009

$$\rho = 2.278 - 10.58(a/Mw) - 4.775(b/Mw) - 6.763(c/Mw) \\ + 0.1188\rho^{+}_{non\text{-}add} - 0.1046\rho^{-}_{non\text{-}add} \tag{2}$$
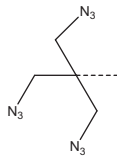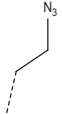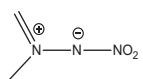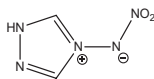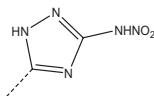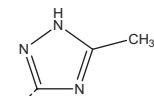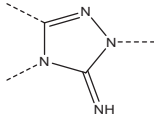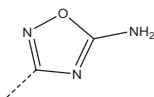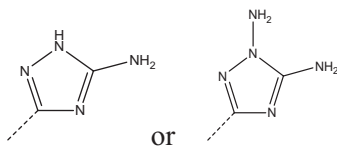
where $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$ are two non-additive correcting functions, which can increase and decrease the density of a high nitrogen compound, respectively. Table 2 provides different values of $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$, which have been derived by tedious work on the basis of the following steps:

1) *Specification of common functional groups and molecular fragments between different high nitrogen organic compounds*. The effects of common functional groups and molecular fragments, confirmed in previous studies [32-35, 37, 38], which may give large deviations from those obtained by the contributions of elemental composition.

2) *Adjustment of the best values for $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$*. These data were obtained by regression of different quantities for $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$ to give the highest value of R^2 and lowest the root-mean-square deviation (*RMSD*).

Thus, the functional groups and molecular fragments listed in Table 2 were specified for some derivatives of high nitrogen organic compounds that show large positive or negative deviations from Equation 1. Details of the derivation method have been illustrated elsewhere [84]. For those high nitrogen organic compounds that do not contain the functional groups listed in Table 2, the values of $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$ are zero.

Table 2.   The values of $\rho^{+}_{non\text{-}add}$ and $\rho^{-}_{non\text{-}add}$

$\rho^{-}_{non\text{-}add}$			
Molecular moieties	$\rho^{-}_{non\text{-}add}$	Examples	Comments
–N(R)(NO$_2$ or NO)	1.2		–
–CN	0.5		The attachemnt of –CN to heterocyclic ring.
–OR	1.1		The attachment of –OR to tetrazole ring.

	1.3		The attachment of three $(CH_2)_n$-N_3 to tertiary carbon.
$-N_3$	0.5		The attachment of more than two $-(CH_2)_n-N_3$ to heterocyclic rings.

$\rho^+{}_{non\text{-}add}$			
Molecular moieties	$\rho^+{}_{non\text{-}add}$	Examples	Comments
	0.6		–
$-NH-NO_2$	0.9		The attachment of more than one -NH-NO$_2$ to triazole rings without other substituents.
$-NH-$	1.6		The presence of more than two $-NH-$ groups without substituents in ring case.
$-R$	1.9		The attachment of more than one $-R$ groups to triazole rings.
=NH (cyclic)	1.0		–
	1.0		The attachment of more than two $-NH_2$ groups to oxadiazole rings.
$-NH_2$	1.4	or	The attachment of more than one $-NH_2$ group to triazole rings without other substituents or $-N=N-$ between two triazole rings.

3 Results and Discussion

3.1 Statistical assessment of Equation 2

Due to the uncertainty of experimental data, the value of R^2 for Equation 2 was 0.878, which shows an improvement with respect to Equation 1. The standard deviation (*SD*) of the new model estimates the deviation of predictions with respect to the experimental values. The value of *SD* for Equation 2 was equal to 0.047 g·cm^{-3}, where $F = 165.1$ and the significance of $F = 5.14\text{E}{-}51$, which is lower than the value calculated for Equation 1, *i.e.* 0.076 g·cm^{-3}.

Table 3 provides the statistical parameters for five variables of Equation 2. The values of the standard deviations (*sd*) for these variables indicate whether or not the individual variables are significant in predicting the density. Thus, the contribution of a specified variable is significant if its standard deviation is small relative to the coefficient [85]. The *P*-value is another statistical parameter that gives the probability that a parameter estimated from the measured data should have the value that was determined. If the *P*-value for a variable is less than 0.05, the effect of that variable is significant and the observed effect is not due to random variations. As indicated in Table 3, all of the five variables given in Equation 2 have suitable statistical parameters because they have a highly significant impact in the development of Equation 2.

Table 3. Regression coefficients, standard deviations (*sd*), *P*-values, and confidence intervals of the best linear regression model

	Coefficient	*sd*	*P*-value	Lower limit (95%)	Upper limit (95%)
Intercept	2.278	0.035	1.79E–92	2.208	2.348
a/Mw	−10.58	0.810	1.49E–24	−12.19	−8.981
b/Mw	−4.775	0.322	1.41E–28	−5.412	−4.137
c/Mw	−6.763	0.651	2.93E–18	−8.053	−5.473
$\rho^+_{non\text{-}add}$	0.1188	0.011	2.55E–19	0.0970	0.1405
$\rho^-_{non\text{-}add}$	−0.1046	0.018	7.06E–08	−0.1405	−0.0686

3.2 Comparison of the reliability of the new model with two complex quantum mechanical approaches

A suitable method using quantum-mechanically determined molecular volumes (V_M) of an isolated molecule has been developed for estimating the densities of neutral molecules as [20]:

$$\rho = Mw_{molecule}/V_M \tag{3}$$

where $Mw_{molecule}$ is the molecular mass of the molecule and V_M is the volume inside the 0.001 a.u. isosurface of electron density surrounding the molecule, calculated using density functional theory (DFT) at the B3LYP/6-31G** level [86] with the Gaussian program package [87]. It was indicated that adding corrections for electrostatic interactions can be done to better represent the intermolecular interactions in neutral CHNO crystals as [88]:

$$\rho = \alpha_1(Mw_{molecule}/V_M) + \beta_1(v\sigma^2_{tot}) + \gamma_1 \tag{4}$$

where σ^2_{tot} is the total variance of the electrostatic potential on the 0.001 a.u. molecular surface; the parameter v quantifies the degree of balance between the positive and negative potentials on the molecular surface; the three parameters α_1, β_1 and γ_1 were found through least squares fitting to experimental information.

Table 4 compares the predicted results from Equations 1 and 2 with the output from the quantum-mechanical approaches of Equations 3 and 4, which have been computed by Rice and Byrd [22] for a further 32 high nitrogen organic compounds as a test set. Table 5 provides the different statistical parameters of Equations 1 and 2 as compared to the complex methods given in Equations 3 and 4. Five statistical parameters are listed in Table 5, *viz* the average deviation (*AD*), *SD*, absolute maximum deviation (*AD*max), average absolute deviation (*AAD*), absolute maximum deviation (*AD*max) and average absolute relative deviation (*AARD%*). *AD* measures accuracy, which defines the value of bias and systematic errors. As mentioned before, *SD* is a measure of precision, which can be used to determine the spread of data around the regression model. *AD*max is another measure of precision because it determines the worst error in the predictions. *AAD* is a linear measure of errors, which show the average size of errors. *AARD%* provides an easy way of judging the extent, or importance of errors, which facilitates relative comparisons among various methods. If the ratio of *SD/AAD* approaches 1.25, it shows that the errors are distributed in a normal pattern. For a heavily-tailed distribution of errors, the *SD/AAD* ratio approaches 1.71 [89]. The values of the *SD/AAD* ratio for Equation 1, Equation 2, Equation 3 and Equation 4 were 1.26, 1.29, 1.19 and 1.2, respectively. All of the statistical parameters in Table 5 confirm that Equation 2 is an improvement over Equation 1, where the results are unbiased and free from systematic errors. Equations 2 and 4 can predict the density of high nitrogen compounds with adequate accuracy and precision.

Table 4. Comparison of the predicted results of Equations 1 and 2 for high nitrogen organic compounds with experimental data (g·cm⁻³), as well as the output from the quantum-mechanical approaches of Equations 3 and 4, which have been computed by Rice and Byrd [22]

| Name	Composition	Exp. [47]	N%	Equation 1	Dev	Equation 2	Dev	Equation 3	Dev	Equation 4	Dev
3-Amino-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine	$C_7H_9N_7$	1.449	51.29	1.433	−0.016	1.417	−0.032	1.414	1.367	1.452	0.003
1-Phenyl-5-(azido)-1H-tetrazole	$C_7H_5N_7$	1.515	52.39	1.528	0.0126	1.501	−0.014	1.487	1.460	1.463	−0.052
4,4',6,6'-Tetra-azido-2,2'-azo-1,3,5-triazine (triclinic beta)	C_6N_{20}	1.674	79.53	1.744	0.0702	1.713	0.039	1.713	1.713	1.696	0.022
4,4',6,6'-Tetra-azido-2,2'-azo-1,3,5-triazine (orthorhombic alpha)	C_6N_{20}	1.704	79.53	1.744	0.0402	1.713	0.009	1.718	1.718	1.689	−0.015
4,4',6,6'-Tetra-azido-2,2'-hydrazo-1,3,5-triazine	$C_6H_2N_{20}$	1.649	79.08	1.718	0.0685	1.689	0.040	1.703	1.697	1.678	0.029
1,4-Bis-[1-methyltetrazol-5-yl]-1,4-dimethyl-2-tetrazene	$C_6H_{12}N_{12}$	1.473	66.65	1.486	0.0132	1.476	0.003	1.458	1.410	1.433	−0.040
N,N-Dimethyl-N'-(5-methyltetrazol-1-yl)formamidine	$C_5H_{10}N_6$	1.328	54.53	1.366	0.0376	1.361	0.033	1.306	1.241	1.297	−0.031
N,N-Bis(1-H-3-methyl-tetrazol-5-yl)-methylamine	$C_5H_9N_9$	1.4901	64.6	1.485	−0.005	1.474	−0.016	1.458	1.412	1.441	−0.049
N,N-Bis(1-H-3-methyl-tetrazol-5-yl)-amine	$C_4H_7N_9$	1.50783	69.6	1.537	0.0288	1.523	0.015	1.495	1.456	1.482	−0.026
2,2'-Dimethyl azotetrazolate	$C_4H_6N_{10}$	1.48	72.15	1.58	0.1002	1.563	0.083	1.520	1.489	1.517	0.037
2,2'-Dimethyl-5,5'-azotetrazole	$C_4H_6N_{10}$	1.515	72.15	1.58	0.0652	1.563	0.048	1.522	1.491	1.520	0.005
4,5-Dicyano-1H-1,2,3-Triazole	C_4HN_5	1.554	58.8	1.632	0.0782	1.545	−0.009	1.505	1.497	1.544	−0.010
1-Hydroxyethyl-5-aminoterazole	$C_3H_7N_5O$	1.511	54.25	1.506	−0.005	1.510	−0.001	1.437	1.383	1.499	−0.012

Name	Composition	Exp. [47]	N%	Equation 1	Dev	Equation 2	Dev	Equation 3	Dev	Equation 4	Dev
1-Methyl-5-(methylamino)-1H-tetrazole	$C_3H_7N_5$	1.381	61.93	1.406	0.0246	1.402	0.021	1.330	1.268	1.378	−0.003
1-Azidoethyl-5-aminotetrazole	$C_3H_6N_8$	1.4763	72.71	1.547	0.0703	1.534	0.058	1.466	1.427	1.501	0.025
1-Methyl-5-(methylnitrosoamino)-1H-tetrazole	$C_3H_6N_6O$	1.444	59.14	1.568	0.1244	1.441	−0.003	1.485	1.443	1.446	0.002
5,6-Dihydro-1H-imidazo[1,2-d]tetrazole	$C_3H_5N_5$	1.524	63.05	1.485	−0.039	1.472	−0.052	1.462	1.417	1.497	−0.027
7-Nitro-5,6-dihydro-7H-imidazolo[1,2-d]tetrazole	$C_3H_4N_6O_2$	1.69	53.84	1.693	0.0032	1.692	0.002	1.667	1.641	1.715	0.025
7-Nitroso-5,6-dihydro-7H-imidazolo[1,2-d]tetrazole	$C_3H_4N_6O$	1.647	59.99	1.634	−0.013	1.625	−0.022	1.594	1.565	1.628	−0.019
2,4,6-Triazido-1,3,5-triazine	C_3N_{12}	1.736	82.34	1.754	0.0184	1.724	−0.012	1.690	1.690	1.648	−0.088
N-Methyl-1H-tetrazol-5-amine	$C_2H_5N_5$	1.479	70.69	1.488	0.009	1.481	0.002	1.397	1.346	1.463	−0.016
1-Methyl-5-nitriminotetrazole	$C_2H_4N_6O_2$	1.716	58.33	1.713	−0.003	1.716	0.000	1.638	1.610	1.658	−0.058
2-Methyl-5-nitriminotetrazole	$C_2H_4N_6O_2$	1.667	58.33	1.713	0.0459	1.716	0.049	1.617	1.589	1.606	−0.061
3,6-Diamino-1,2,4,5-tetrazine	$C_2H_4N_6$	1.611	74.99	1.569	−0.042	1.556	−0.055	1.506	1.470	1.524	−0.087
5-Azido-1-methyl-2H-tetrazole	$C_2H_3N_7$	1.533	78.39	1.633	0.1005	1.615	0.082	1.520	1.496	1.494	−0.039
1,2,4-Triazole	$C_2H_3N_3$	1.456	60.85	1.484	0.0278	1.469	0.013	1.377	1.334	1.432	−0.024
s-Tetrazine	$C_2H_2N_4$	1.501	68.28	1.595	0.0943	1.573	0.072	1.470	1.446	1.435	−0.066
3,6-Diazido-1,2,4,5-tetrazine	C_2N_{10}	1.719	85.36	1.765	0.0462	1.736	0.017	1.686	1.686	1.659	−0.060
N,N'-Diaminourea	CH_6N_4O	1.518	62.22	1.52	0.0024	1.541	0.023	1.395	1.328	1.454	−0.064
5-Nitriminotetrazole	$CH_2N_6O_2$	1.894	64.61	1.809	−0.085	1.811	−0.083	1.765	1.750	1.841	−0.053
1H-1,2,3,4-Tetrazole	CH_2N_4	1.529	79.99	1.619	0.0899	1.604	0.075	1.486	1.457	1.563	0.034
Tetrazole azide	CHN_7	1.67	88.28	1.736	0.0657	1.713	0.043	1.628	1.619	1.701	0.031

Thus, the reliability of the simple model of Equation 1 is close to Equation 3. Moreover, the improved correlations 2 and 4 can make predictions that are more reliable than Equations 1 and 3. Comparison between the predicted values from the simple models of Equations 1 and 2, as well as from the complex quantum mechanical approaches of Equations 3 and 4, with experimental data is also indicated in Figure 1.

Table 5. Comparison of the statistical parameters of Equations 1 and 2 with the output from the quantum-mechanical approaches of Equations 3 and 4, which have been computed by Rice and Byrd [22] for 32 high nitrogen organic compounds

Model	AD [g·cm^{-3}]	SD [g·cm^{-3}]	AD_{max} [g·cm^{-3}]	AAD [g·cm^{-3}]	$AARD\%$
Equation 1	0.032	0.057	0.124	0.045	2.903
Equation 2	0.013	0.042	0.083	0.032	2.057
Equation 3	0.035	0.056	0.129	0.047	3.007
Equation 4	−0.021	0.042	0.088	0.035	2.191
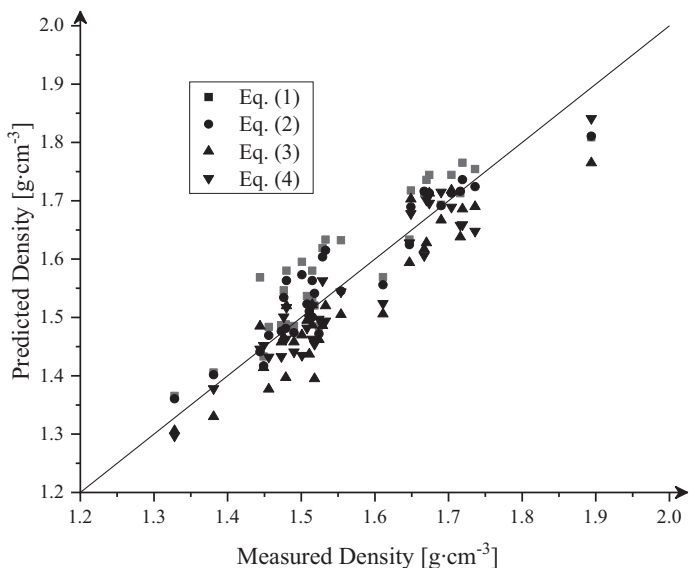
Figure 1. Comparison between the predicted values from the simple models of Equations 1 and 2, as well as the complex quantum mechanical approaches of Equations 3 and 4, with experimental data

4   Conclusions

A reliable approach was introduced for the prediction of the density of high nitrogen organic compounds (>50 wt.% N) at or near room temperature. Equation 1 is a core correlation, which is based on elemental composition, for the prediction of the density, and its reliability was improved by considering $\rho^+_{non-add}$ and $\rho^-_{non-add}$ in Equation 2. These equations can be applied for different types of high nitrogen organic compounds, including triazole, tetrazole, triazine, tetrazine, furazan, and some of organic nitrogen-containing chains. The reliability of these equations was compared with the output from two complex quantum mechanical models. The former facilitate the calculation of densities of different high nitrogen compounds, without the need to use complicated expensive computer programs, as well as expert operators. Thus, the present method provides the simplest and easiest procedure and at the same time gives reliable results relative to complex quantum mechanical methods.

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