

Theoretical studies on the heats of formation, densities, and detonation properties of substituted s-tetrazine compounds

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Abstract Substituted s-tetrazine compounds were designed and investigated in order to find comprehensive relationships between the structures and performances of high-nitrogen energetic compounds. Density functional theory (DFT) was used to predict the optimized geometries, electronic structures, heats of formation and densities, and the detonation properties were evaluated by using the VLW equation of state (EOS). Calculation results show that there are good linear relationships between heats of formation, densities, detonation properties and the number of N atom in all designed high-nitrogen compounds. Furthermore, several designed high-nitrogen compounds show good detonation velocities and pressures compared with octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), making them potential candidates for high-energy-density materials (HEDM).

Keywords Detonation properties · Heats of formation · HEDM · High-nitrogen · VLW

Introduction

Despite energetic materials belong to the category of the most hazardous material, their roles in the civil and

military fields are very important. To ensure the durative development of these fields, the search for new energetic materials is still an unalterable goal for explosive researchers. Modern high-energy-density materials (HEDM) derive most of their energies either (i) from oxidation of the carbon backbone, as with traditional explosives containing C, H, N, O atoms such as TNT, RDX, HMX, CL-20 and TEX [1–3] or (ii) from their very high positive heats of formation [4] in such high-nitrogen energetic materials [5–7] as 2,4,6-tri(azido)-1,3,5-triazine (TAT); 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine(TAHT); 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) and 2,5,8-tri(azido) -s-heptazine(TAH) [8]. In recent years, high-nitrogen energetic compounds have attracted great attentions for their large positive heats of formation, and this advantage makes them promising HEDMs, as illustrated by the recent examples of 3,3'-Azobis(6-Amino-s-Tetrazine) (DAAT) [5, 6] and 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz) [7]. To find new high-nitrogen energetic materials and obtain a comprehensive picture of their high explosive performances, a series of substituted s-tetrazine compounds are designed in this work, and their geometries, electronic structures, heats of formation (HOF), densities (ρ), explosive performances are investigated by theoretical methods.

Methods and computational details

Study contents

In general, there are three structural units (containing parent structure, linkage bridge, and substituent) in the high-nitrogen energetic molecules, such as BTATz [7]

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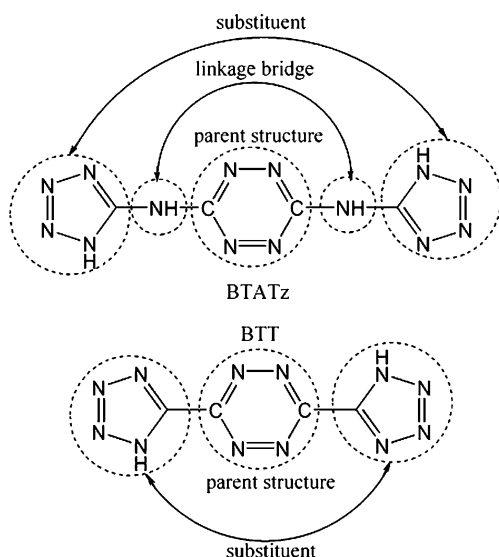


Fig. 1 The structural characteristics of different high-nitrogen compounds

(Fig. 1). However, there exist exceptions which have no linkage bridge, for instance, BTT [9] (Fig. 1). Based on the structural principle of the latter, and taking s-tetrazine (T) as the parent structure and azolyl groups (five-membered aromatic rings with different numbers of nitrogen atoms) (Fig. 2) as the substituents, 18 substituted s-tetrazine compounds were designed as shown in Fig. 3 (To the best of our knowledge, T2M1 and T2M2 of these compounds have been synthesized [10]). The optimized geometries show that s-tetrazine and azolyl rings are coplanar, but the tetrazole rings in TM8 and T2M8 are out of plane by 24.9° and 23.3°, respectively; and the pentazole rings in TM9 and T2M9 are also out of plane by 30.8° and 27.4°, respectively (Fig. 3c). Based on the optimized geometries, the other properties of all designed compounds, such as heats of formation, densities, detonation velocities and pressures, were calculated and discussed below.

Densities calculations

An efficient and convenient method based on the quantum chemical computations was used to predict the densities of energetic materials [11, 12]. The density was obtained from the molecular volume divided by the molecular weight, while the molecular volume of each molecule was yielded from the statistical average value of 100 single-point molar volume calculations on each optimized structure. The molar volume was calculated by the Monte-Carlo method in the Gaussian03 program package [13], which is defined as inside a contour of 0.001 e/Bohr³ density.

Heats of formation (HOF) calculations

The calculation of HOF was based on atomization scheme [14, 15]. The HOF of a molecule M(C_xH_yN_z) being considered contain only carbon, nitrogen and hydrogen, is defined as the enthalpy change following scheme 1:

Where x, y or z is the molar ratio of the atom in the molecule (M), the superscript “0” and the subscript “g” represent the standard state and the gas phase, respectively. In the atomization scheme, HOF of M at 298 K can be written as Eq. 1:

$$\begin{aligned} \Delta H_f^{298} &= \Delta H_r^{298} + \sum_A \Delta H_{\text{exp}}^{298}(A^0 \rightarrow A_g) \\ &= \Delta E^{298} + \Delta(PV) + \sum_A \Delta H_{\text{exp}}^{298}(A^0 \rightarrow A_g) \\ &= \Delta E_0 + \Delta ZPVE + \Delta H_T + \Delta nRT + \sum_A \Delta H_{\text{exp}}^{298}(A^0 \rightarrow A_g) \end{aligned} \quad (1)$$

The single-point energy (E_0) was calculated at the B3LYP/6-311+G(2df,2p)//B3LYP/6-311G** level, while the corrected enthalpy from 0 to 298 K (H_T) and zero point vibration energy (ZPVE) were calculated at B3LYP/6-311G** level. In Eq. 1, the last term represents the experimental heat of formation of atom A from the standard

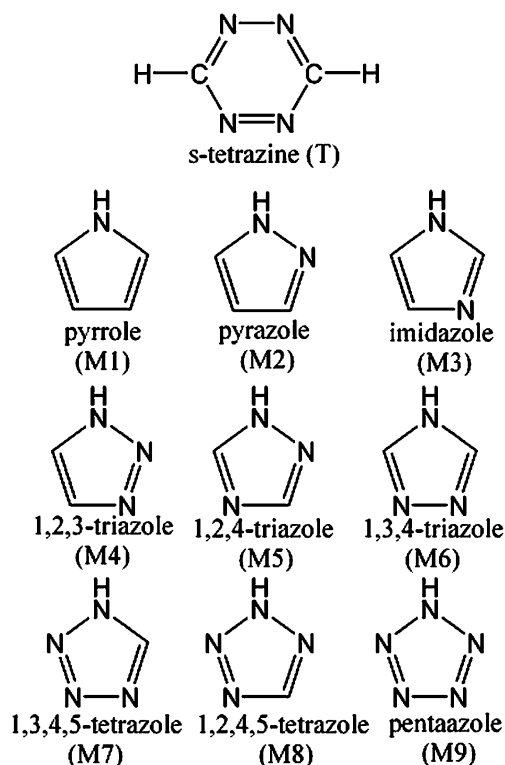


Fig. 2 The geometry of all azolyl groups and s-tetrazine(T)

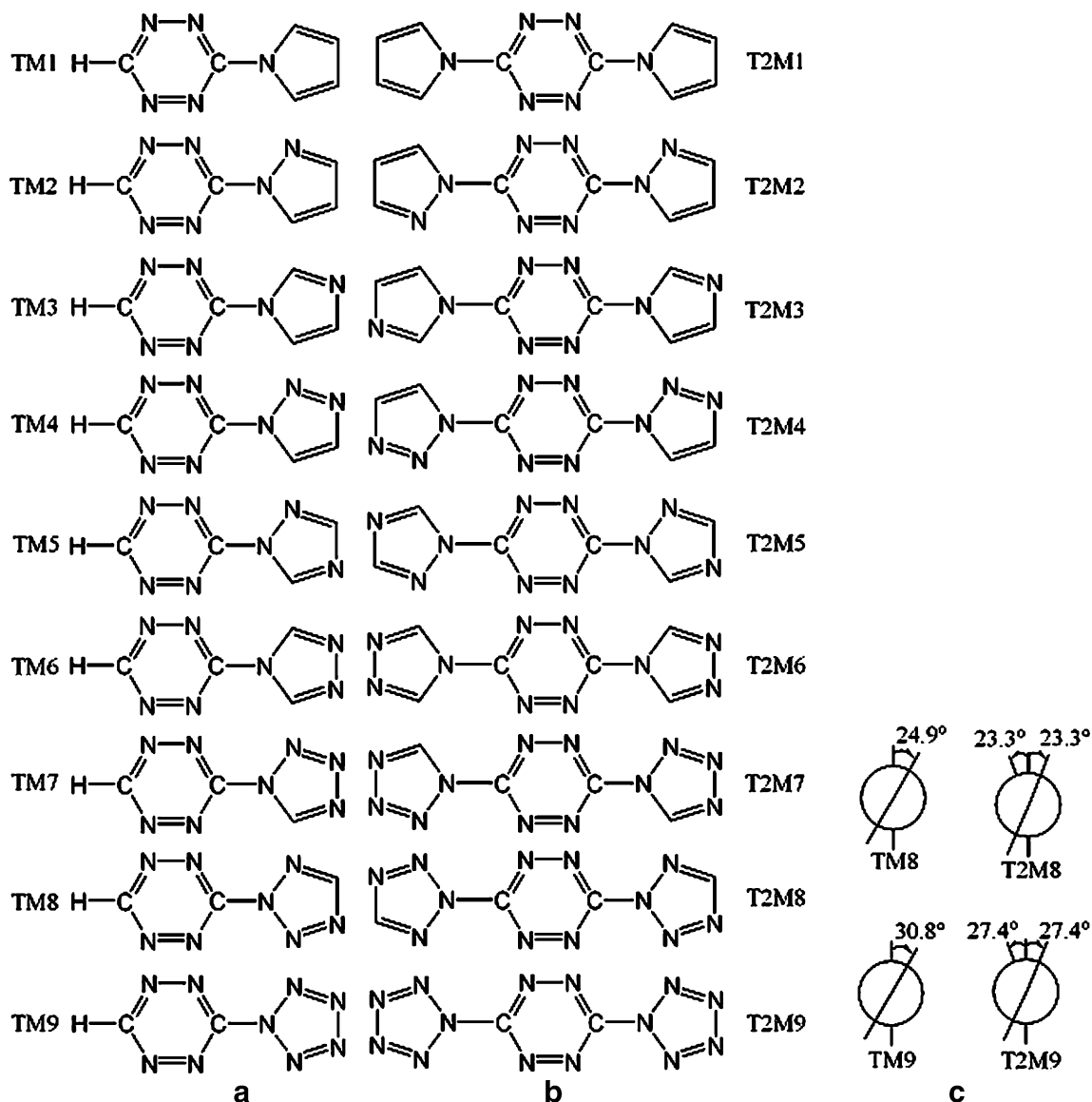


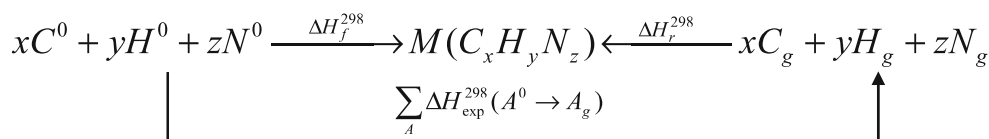
Fig. 3 The geometries of all substituted s-tetrazine compounds. (a) the single substituted compounds; (b) the double substituted compounds; (c) lateral view

state to gaseous state at 298 K, which can be found from ref. [16]. Finally, the HOF values were calculated by our developed program based on the atomization scheme.

Detonation properties calculations

All detonation properties were calculated by our developed VLW code including the VLW EOS (Scheme 2) [17], law

of mass conservation, law of momentum conservation, law of energy conservation and C-J detonation conditions [18]. In the scheme 2, N is Avogadro Constant, k is Boltzmann constant and T^* the nondimensional temperature, σ and ϵ are both the Lennard-Jones potential parameters. Compared with BKW method with empirical constants [18], the VLW EOS only needs the chemical compositions, heats of formation, and densities



Scheme 1 The atomization scheme

$$\frac{pV}{RT} = 1 + B^*(T^*)w + \frac{B^*(T^*)}{T^{*1/4}} \sum_{n=3}^m \frac{w^{(n-1)}}{(n-2)^n}$$

$$B^*(T^*) = \sum_{j=0}^{\infty} b^{(j)} T^{*-(2j+1)/4}$$

$$b^{(j)} = -\frac{2^{j+1/2}}{4j!} \Gamma\left(\frac{2j-1}{4}\right)$$

$$b_0 = \frac{2}{3} \pi N \sigma^3$$

$$T^* = \frac{kT}{\varepsilon}$$

$$w = \frac{b_0}{V}$$

Scheme 2 The VLW equation of state

of compounds as input and can compute the detonation velocities, pressures and heats of the solid, liquid and gaseous explosives and propellants.

Results and discussion

Electronic structures

The net charge distribution was calculated by the natural bond orbital (NBO) method. Table 1 illustrates the total charge (Tc), which is the summation of the charge in s-tetrazine ring and unsubstituted H atom for single substituted compounds (Fig. 3a), and s-tetrazine ring for double substituted compounds (Fig. 3b), respectively. From Table 1, the decreases of total charge indicate that there are electrons delocalizations and therefore charge transfer between the tetrazine ring and azolyl groups, which also indicates strong interactions between them. In order to study this interaction, the stabilization interaction energy (E_2) was calculated by the second-order perturbation theory. In the NBO analysis, E_2 is used to describe the delocalization trend of electrons from the donor bond to the acceptor bond. Table 2 lists the values of E_2 that represent the interactions between the lone pairs of N atom connected with s-tetrazine and the nearest C-N antibonding orbital of s-tetrazine. As shown in Table 2, there are strong donor-acceptor interactions among these systems, and the interaction energies decrease with the increase of N atom except for TM6 and T2M6. This indicates that substituted s-tetrazine compounds contain

Table 1 Total charge of s-tetrazine

| | Tc | | Tc |
|-----|---------------------|------|---------------------|
| T | -0.196 ^a | T | -0.390 ^a |
| TM1 | 0.074 | T2M1 | 0.178 |
| TM2 | 0.112 | T2M2 | 0.242 |
| TM3 | 0.102 | T2M3 | 0.210 |
| TM4 | 0.142 | T2M4 | 0.280 |
| TM5 | 0.136 | T2M5 | 0.270 |
| TM6 | 0.127 | T2M6 | 0.244 |
| TM7 | 0.165 | T2M7 | 0.308 |
| TM8 | 0.187 | T2M8 | 0.352 |
| TM9 | 0.216 | T2M9 | 0.388 |

^a means the charge for s-tetrazine without one or two H atoms, respectively

a large conjugation system, which is a good indication for their stability [19].

HOMO and LUMO

HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The analysis of the molecular orbital can provide much useful information [20] and the difference of the energies of the HOMO and LUMO, termed the band gap, is in close agreement with λ_{\max} values from UV spectroscopy. The calculated results of the HOMO and LUMO energies are listed in Table 3. Compared with s-tetrazine (T), it is noted that the single orbital energies and $\Delta E_{\text{HOMO-LUMO}}$ ($E_{\text{HOMO}} - E_{\text{LUMO}}$) of substituted s-tetrazine compounds increases, implicating a shift toward higher frequencies in their electronic absorption spectra.

Table 2 The part of E_2 for all 18 compounds (kJ mol⁻¹)

| | E_2 | | E_2 |
|-----|--------|------|--------|
| TM1 | 234.72 | T2M1 | 227.90 |
| TM2 | 204.89 | T2M2 | 203.72 |
| TM3 | 221.54 | T2M3 | 219.24 |
| TM4 | 190.83 | T2M4 | 188.99 |
| TM5 | 189.24 | T2M5 | 193.09 |
| TM6 | 208.11 | T2M6 | 211.67 |
| TM7 | 179.45 | T2M7 | 185.35 |
| TM8 | 135.90 | T2M8 | 137.78 |
| TM9 | 114.14 | T2M9 | 128.41 |

Table 3 The HOMO and LUMO energies and the energy gap for all the molecules (eV)

| T | | TM1 | TM2 | TM3 | TM4 | TM5 | TM6 | TM7 | TM8 | TM9 |
|-------------------------------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| E_{HOMO} | -6.94 | -0.240 | -0.253 | -0.259 | -0.266 | -0.266 | -0.277 | -0.280 | -0.272 | -0.288 |
| E_{LUMO} | -3.29 | -0.119 | -0.121 | -0.130 | -0.134 | -0.133 | -0.143 | -0.147 | -0.139 | -0.154 |
| $\Delta E_{\text{HOMO-LUMO}}$ | -3.65 | -0.121 | -0.132 | -0.129 | -0.132 | -0.133 | -0.134 | -0.133 | -0.133 | -0.132 |
| T | | T2M1 | T2M2 | T2M3 | T2M4 | T2M5 | T2M6 | T2M7 | T2M8 | T2M9 |
| E_{HOMO} | -6.94 | -0.236 | -0.254 | -0.258 | -0.276 | -0.276 | -0.291 | -0.301 | -0.286 | -0.314 |
| E_{LUMO} | -3.29 | -0.112 | -0.123 | -0.140 | -0.145 | -0.144 | -0.163 | -0.169 | -0.153 | -0.180 |
| $\Delta E_{\text{HOMO-LUMO}}$ | -3.65 | -0.124 | -0.131 | -0.118 | -0.131 | -0.132 | -0.128 | -0.132 | -0.133 | -0.134 |

Detonation properties

Firstly, the heat of formation (HOF) and density (ρ) were computed by atomization scheme and Monte-Carlo method discussed above, respectively. Then the detonation velocity (V_D) and pressure (P_D) were calculated by the VLW EOS based on the above parameters. At last, the corresponding results are shown in Table 4.

Because NN bond has more contribution to the heats of formation in high-nitrogen compounds [21], TM2, T2M2, TM4, T2M4, TM7 and T2M7 (containing more NN bonds than their isomers) are chosen as the objective compounds from the aspect of obtaining more energies. From Table 4, it is found that the number of N atom has a significant influence on detonation velocities and pressures of the objective compounds, but the number of substituents shows little influence. For instance, the detonation properties of T2M1 with two pyrroles as substituents are lower than that of TM1 with only one pyrrole as substituent. The more clear relations between the N atom numbers and the properties were plotted in the Figs. 4 and 5, where R is the correlation coefficient and SD is the standard deviation. As shown in the four figures, all substituted s-tetrazine compounds have a good linear relationship between the number of N atoms and the properties with all R values close to 1, which strongly indicating that HOF, ρ , V_D and P_D increase with increasing N atoms, as a whole.

In addition, Table 4 shows that the detonation velocities of TM7, T2M7, and TM9 are close to HMX ($V_D=8.92 \text{ km s}^{-1}$

and $P_D=39 \text{ GPa}$ when $\rho=1.854 \text{ g cm}^{-3}$) [22]. Encouragingly, the V_D of T2M9 is higher than HMX, and the P_D is close to HMX. However, the calculated densities of all designed high-nitrogen compounds are far less than that of HMX, so these compounds can show greater potential if improving their densities. For example, oxidization of N atoms in the compounds by the Caro's acid [7] or the introduction of linkage bridge (such as -NH-, -N=N-) [8] can improve the density effectively.

Conclusions

In this paper, 18 substituted s-tetrazine compounds were designed, and their optimized geometries, electronic structures, heats of formation, densities and explosive performances were investigated by the theoretical methods. The results show that i) when hydrogen atoms of s-tetrazine are substituted by azolyl groups, part of electrons shift to the substituents from s-tetrazine ring; ii) there is a strong donor-acceptor interaction between the direct connected two rings; iii) the HOMO-LUMO gaps increase when azolyl groups are attached to the s-tetrazine ring; iv) there are good linear relationships between the properties and the number of N atoms, the detonation properties would boost up linearly along with the increase of N atoms. Several of the compounds presented in this study exhibit high detonation velocities and pressures, and they can be considered as potential candidates for HEDM.

Table 4 The data for HOF (kJ mol⁻¹), ρ (g cm⁻³), V_D (km s⁻¹) and P_D (GPa) of the objective molecules

| | N atom | HOF | ρ | V_D | P_D | | N atom | HOF | ρ | V_D | P_D |
|-----|--------|-------|--------|-------|-------|------|--------|--------|--------|-------|-------|
| TM1 | 5 | 606.8 | 1.429 | 6.1 | 11.1 | T2M1 | 6 | 766.0 | 1.406 | 5.5 | 6.8 |
| TM2 | 6 | 677.1 | 1.492 | 6.8 | 14.4 | T2M2 | 8 | 904.6 | 1.488 | 6.4 | 12.6 |
| TM4 | 7 | 759.8 | 1.545 | 7.4 | 18.2 | T2M4 | 10 | 1067.1 | 1.590 | 7.5 | 18.5 |
| TM7 | 8 | 825.0 | 1.620 | 8.2 | 23.3 | T2M7 | 12 | 1201.1 | 1.682 | 8.5 | 25.5 |
| TM9 | 9 | 947.9 | 1.677 | 8.8 | 28.0 | T2M9 | 14 | 1450.6 | 1.787 | 10.0 | 37.5 |

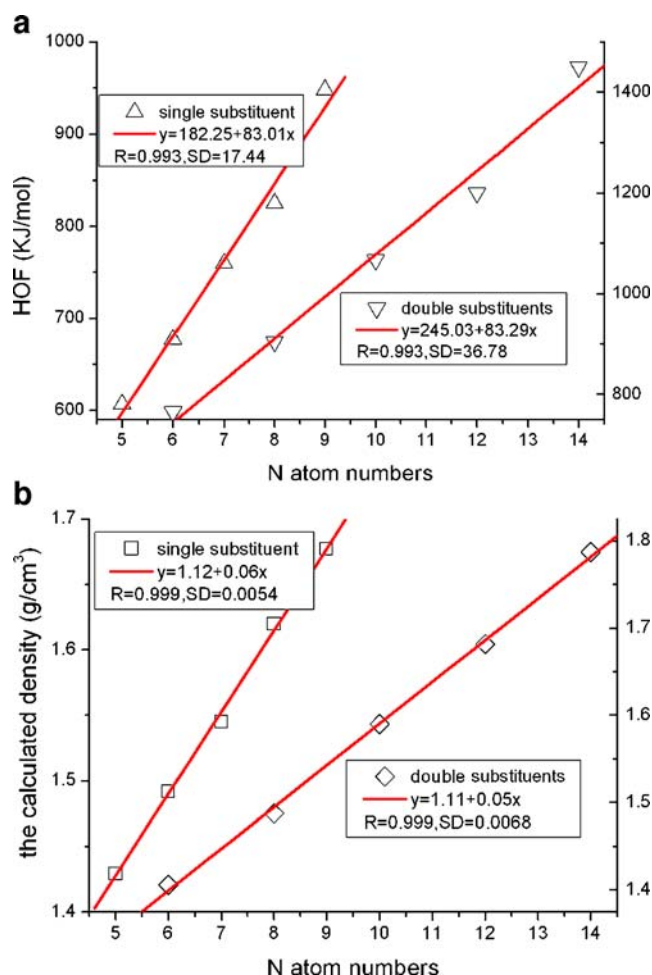


Fig. 4 The relations of HOF, ρ and N atom numbers

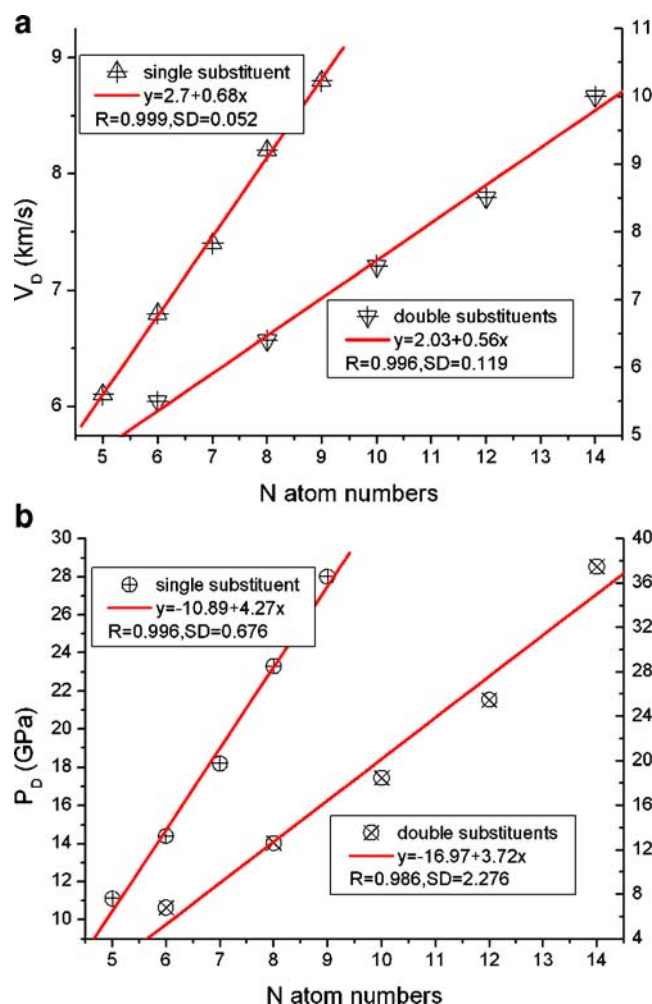


Fig. 5 The relations of V_D, P_D and N atom numbers

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