

Theoretical study on novel nitrogen-rich energetic compounds of bis(amino)-azobis(azoles) with tetrazene unit

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Abstract Six stereoisomers of 5,5'-bis(amino)-1,1'-azobis(tetrazoles) and 30 other structures, including all possible bis(amino)-azobis(azoles) with an N–N=N–N unit, were designed. The molecular geometries were fully optimized at the DFT-B3LYP level with the 6-31++g (d, p) basis set. From the absence of any imaginary frequency in the infrared vibration frequency spectrum, it is predicted that all these studied structures may exist in stable forms. The results of the total energies of the stereoisomers of 5,5'-bis(amino)-1,1'-azobis(tetrazoles) indicate that the two symmetric trans-form structures are more likely to exist than the other four. The pyrolysis process, chemical stability and molecular electrostatic potential were studied via the investigation of their electronic structure. Heats of formation (HOFs) were calculated using the atomization energy method based on the results of the harmonic vibration frequencies, and a linear relationship was found between the HOF and nitrogen chain or nitrogen content. Densities of the title compounds were predicted with the Monte Carlo method. Finally, according to the results of the calculated HOFs and densities, the explosive parameters of these compounds were calculated using the Kamlet–Jacobs formula. 5,5'-

Bis(amino)-1,1'-azobis(tetrazoles) and its isomer 5,5'-bis(amino)-2,2'-azobis(tetrazoles) may have potential for use as energetic compounds.

Keywords Density function theory · Electronic structures · Energetic properties · Heats of formation · Stereoisomers

Introduction

High nitrogen-contented heterocyclic compounds have attracted increasing attention in the field of energetic materials due to their excellent thermal stability, high heats of formation (HOFs) caused by the high strain energies and the many N–N single or double bonds, and their environmentally friendly properties [1–9]. Azoles and their derivatives are part of these high nitrogen-contented heterocyclic compounds. With fascinating structures and excellent properties, azole-based derivatives, polycyclic compounds, complexes and salts have been intensively studied in an effort to meet the increased demand for new energetic materials [5, 10–18]. Klapötke and his co-workers [19–23] and Shreeve's [17, 24, 25] group have performed lots of studies of nitrogen-rich energetic compounds on the basis of triazole, tetrazole and their derivatives. Talawar et al. [3, 26, 27] and Huynh et al. [28, 29] investigated the coordination complexes of the 5-nitro-tetrazolate anion as potential primary explosives. 1,5-diaminotetrazole has a nitrogen content of 84.8 %, good thermal stability and abundant coordination atoms, and thus has been widely utilized to synthesize complexes. Zhang et al. synthesized a series of coordination compounds using 1,5-diaminotetrazole as the ligand, transition metal ions as the central metal cation, and perchlorate, picrate, styphnate, nitrate, or chloride as the outer ion [30–34]. All of these complexes have

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good properties and offer the potential for application as energetic materials.

With the development of calculation chemistry, theoretical calculation has evolved into a useful method for better understanding structure–property relationships and has been widely used to explore new energetic compounds [35–42]. Zhang et al. [43] studied the effect of the π -stack structure in explosives in reducing sensitivity toward external mechanical stimuli. Li et al. [44] investigated substituted pyrazole derivatives with density functional theory (DFT) and predicted that the HOF of 3,4,5-triazidopyroazole was as high as 1240.6 kJmol⁻¹. Zhang et al. [45] reported their theoretical investigation of the electronic structure and the explosive properties of diazido-tetrazole and its isomers. Politzer et al. [46, 47] have done many works on the method of calculation for the performances of energetic compounds, such as to quantitatively analyze the molecular surfaces, an improved crystal density prediction method. With its high efficiency and safety, theoretical calculation can play an increasingly important role when seeking new energetic compounds.

Coupling two molecules of heterocyclic compounds together provides a good way of obtaining explosives with higher nitrogen content and better properties. It was reported [48] that introducing the azo (–N=N–) linkage into nitrogen heterocyclics can not only improve their HOF but also their stability. In 2010, Li et al. [49] synthesized 1,1'-azobis-1,2,3-triazole with a stable N8 chain by coupling two 1-amino-1,2,3-triazole molecules together, and investigated its thermal stability and photochromic properties. 1,1'-azobis-1,2,3-triazole has a higher HOF than 4,4'-azobis-1,3,4-triazole which has an N–N=N–N structure and this is thought to result from the former having more N–N bonds. Later, 1,10-azobis(tetrazole) was synthesized as a highly energetic nitrogen-rich compound with an N10 chain by Klapötke et al. [19]. A considerable number of studies have confirmed that high nitrogen compounds with N chain perform well as energetic compounds.

Based on the previous studies, we investigated theoretically all the bis(amino)- azobis(azoles) with an N–N=N–N structure. These compounds can be formed when two molecules of bis(amino) azoles (Fig. 1) are coupled together. Since six stereoisomers are thought to exist for each compound, we took 5,5'-bis(amino)-1,1'-azobis(tetrazoles) as an example to

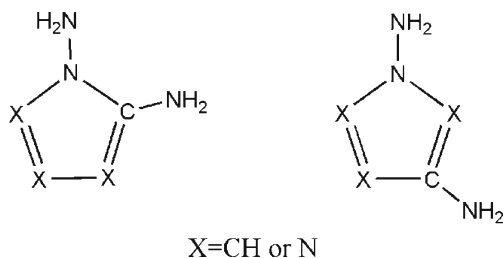


Fig. 1 The general formula of reactant molecules of the title compounds

calculate the total energies of its six stereoisomers and the results showed that two types of configuration possibly exist; hence, we fully optimized these two configuration type of all the bis(amino)- azobis(azoles) (shown in Fig. 2) and tried to determine the most stable configuration of each compound. The fact that no imaginary frequencies were found in the infrared vibration spectra proved that all the investigated structures corresponded to a minimum point on the potential energy surface. Natural bond orbital analyses were undertaken to explore the electronic structures of these compounds. The HOF, density and explosive parameters were calculated to evaluate their potential for use as novel energetic compounds.

Computational methods

The fully optimized molecular structures and infrared vibration frequency were obtained at the DFT-B3LYP [50, 51] level with the 6-31++g(d, p) basis set because of its good performance in geometry, infrared vibration spectra and thermodynamic studies. Single point calculations for the optimized structures were carried out using the MP2 method at the 6-31++g(d, p) level to obtain relatively accurate total energy values [52, 53].

The standard enthalpies of formation of the title compounds were calculated with the following formulas [54]:

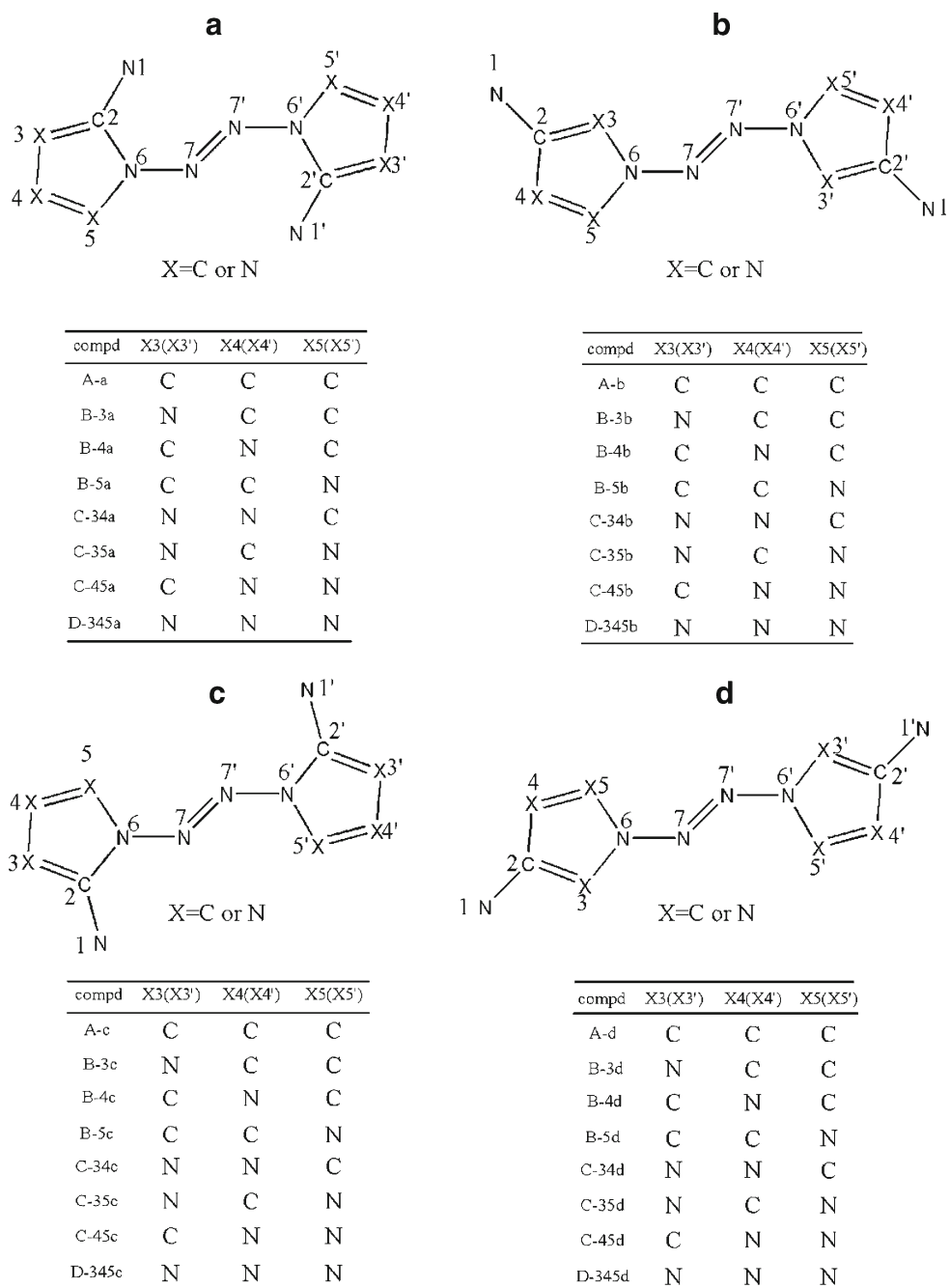
$$\begin{aligned} \Delta_f H^\theta(M, 0K) &= \sum_{atoms} x H_X^\theta(X, 0K) - D_0(M) \\ &= \sum_{atoms} x H_X^\theta(X, 0K) - \left[\sum x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M) \right] \end{aligned} \quad (1)$$

$$\begin{aligned} \Delta_f H^\theta(M, 298K) &= \Delta_f H^\theta(M, 0K) + H_M^\theta(298K) - H_M^\theta(0K) \\ &\quad - \sum_{atoms} x [H_X^\theta(298K) - H_X^\theta(0K)], \end{aligned} \quad (2)$$

where M is the studied molecule, X is the atoms which constitute the molecule, x is the number of X atoms in the M molecules, $D_0(M)$ is the atomization energy of the molecule, which contains the total energies of the molecule ($\varepsilon_0(M)$), the zero-point energy of the molecule ($\varepsilon_{ZPE}(M)$) and the total energies of the constituent atoms ($\sum x \varepsilon_0(X)$), $H_M^\theta(298K) - H_M^\theta(0K)$ is the enthalpy correction for the molecule, and all these values were obtained from the results of the calculations. The values of $H_X^\theta(298K) - H_X^\theta(0K)$ (the enthalpy corrections of the atomic elements) and $H_X^\theta(0K)$ (HOFs of the atoms at 0 K) are from the literature [55, 56].

The bond strength can be evaluated with bond dissociation energy, which is equal to bond dissociation enthalpy for

Fig. 2 Geometric structures and numbering of the compounds (all hydrogen atoms are omitted)



many organic molecules. According to the definition, the bond dissociation enthalpy of the molecule A–B corresponds to the enthalpy of reaction $A-B(g) \rightarrow A(g) + B(g)$. Therefore, at 0 K, the homolytic bond dissociation energy can be calculated by the following terms [57, 58]:

$$\text{BDE}(A-B) = E(A\cdot) + E(B\cdot) - E(A-B). \quad (3)$$

The density of the compound is the ratio of molar mass and molar volume. The molar volume is defined as within a contour of density of $0.001 \text{ e-bohr}^{-3}$, which was evaluated using Monte Carlo integration. Considering the deviation that occurs in volume calculation, 100 single-point calculations

were performed for each optimized structure to obtain a more accurate average volume value.

As the two vital parameters of energetic compounds, the detonation velocity ($\text{km}\cdot\text{s}^{-1}$) and detonation pressure of the title compounds were calculated using the empirical Kamlet–Jacobs (K–J) equations [59]:

$$D = \left(N\bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1.011 + 1.312\rho), \quad (4)$$

$$P = 1.558 N\bar{M}^{1/2} Q^{1/2} \rho^2$$

where D and P denote the detonation velocity ($\text{km}\cdot\text{s}^{-1}$) and detonation pressure (GPa), respectively, N is the

moles of gaseous detonation products per gram of explosive, \bar{M} means the average molecular weight of gaseous products, Q represents the chemical energy of detonation ($\text{cal}\cdot\text{g}^{-1}$), and ρ is the loaded density of explosives ($\text{g}\cdot\text{cm}^{-3}$), although here it is replaced by the computed density. All of these calculations were carried out with the Gaussian03 program package [60]. No symmetry constraints were imposed on the structural optimizations.

Results and discussions

Molecular geometries and total energies

As mentioned previously, six stereoisomers, which result from the cis- or trans-forms caused by N=N and rotation of the five-membered ring, may exist stably when two azoles molecules couple together. Considering the structural similarity of all bis(amino)-azobis(azoles), 5,5'-bis(amino)-1,1'-azobis(tetrazoles) were taken as examples to investigate the possible existence of stereoisomers. Their fully optimized structures at the B3LYP/6-31++G(d,p) level are shown in Fig. 3.

To discuss the relative stability of these isomers, their molecular total energies at MP2/6-31++G(d,p) level were obtained (Table 1). From the results, the conclusion was reached that the stability of these isomers is in the following order: II>I>III>IV>V>VI. Structure II (C_i symmetry) is most likely to exist judging by it having the lowest

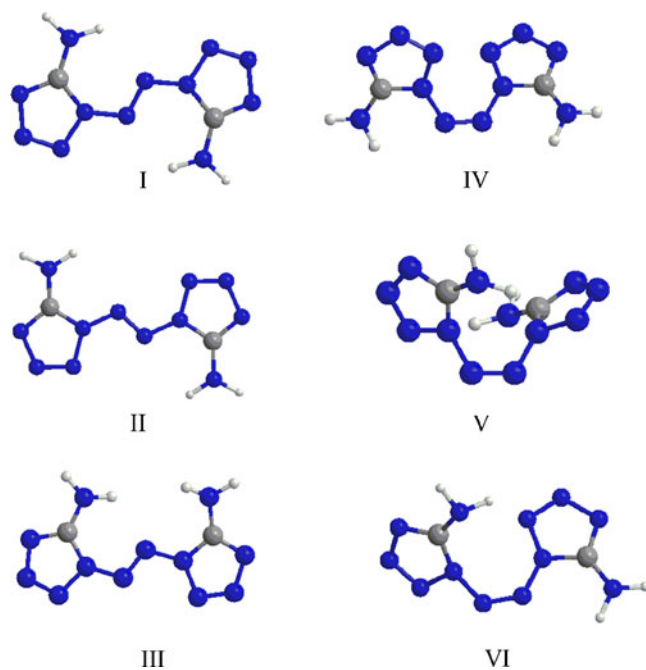


Fig. 3 Six tautomers/rotamers of 5,5'-bis(amino)-1,1'-azobis(tetrazoles) optimized at B3LYP/6-31++G(d, p)

Table 1 Total energies and frontier orbital energy levels and their gaps ($\text{kJ}\cdot\text{mol}^{-1}$)

Compounds	E/MP2($\times 10^3$)	E_{LUMO}	E_{HOMO}	$E_{\text{L-H}}$
A-a	-1666.502	-185.39	-514.03	328.63
A-c	-1666.525	-199.19	-512.90	313.71
A-b	-1666.511	-164.57	-496.95	332.39
A-d	-1666.504	-180.75	-500.57	319.82
B-3a	-1750.400	-235.62	-570.95	335.32
B-3c	-1750.528	-241.03	-570.76	329.74
B-3b	-1750.403	-176.19	-537.50	361.32
B-3d	-1750.398	-213.12	-545.19	332.07
B-4a	-1750.441	-245.62	-577.08	331.47
B-4c	-1750.450	-266.15	-571.81	305.66
B-4b	-1750.495	-222.25	-539.42	317.17
B-4d	-1750.475	-250.34	-541.80	291.47
B-5a	-1750.373	-212.80	-581.12	368.32
B-5c	-1750.393	-203.26	-578.29	375.04
B-5b	-1750.334	-210.99	-547.34	336.35
B-5d	-1750.325	-200.92	-543.85	342.93
C-34a	-1834.291	-307.86	-671.49	363.63
C-34c	-1834.304	-319.64	-669.57	349.93
C-34b	-1834.401	-235.94	-595.42	359.48
C-34d	-1834.384	-280.48	-601.06	320.58
C-35a	-1834.397	-261.70	-638.33	376.64
C-35c	-1834.415	-247.09	-631.77	384.69
C-35b	-1834.193	-234.89	-585.24	350.35
C-35d	-1834.185	-247.03	-587.37	340.33
C-45a	-1834.136	-288.48	-644.13	355.65
C-45c	-1834.143	-284.94	-638.70	353.76
C-45b	-1834.143	-291.34	-609.74	318.40
C-45d	-1834.125	-292.44	-606.83	314.39
D-345a(I)	-1918.020	-348.28	-736.48	388.20
D-345c(II)	-1918.028	-340.04	-727.56	387.52
D-345b	-1918.022	-318.67	-661.05	342.38
D-345d	-1918.002	-338.18	-661.26	323.07
III	-1918.007	/	/	/
IV	-1917.961	/	/	/
V	-1917.932	/	/	/
VI	-1917.947	/	/	/

molecular total energy, which is followed by structure I (C_2 symmetry). Meanwhile, the molecular total energy deviation ($8 \text{ kJ}\cdot\text{mol}^{-1}$) between structure I and II is small, hence, both of them are thought to possibly exist stably. Thus, we fully optimized these two symmetrical trans-form configurations of all bis(amino)-azobis(azoles) (Fig. 2), and their total energies and part of the optimized parameters of these structures are listed in Table 1. Like D-345a (I), all the molecules of group (a) and group (b) have loose C_2 symmetries, while all the structures in group (c) and group (d) have loose C_i symmetries, with the H atoms

of two -NH_2 staying at different sides of the molecular plane.

Table 1 shows that the total energy decreases by $84 \text{ kJ}\cdot\text{mol}^{-1}$ or so when the number of nitrogen atoms in the molecule increases by two, while compounds with the same molecular formula have much less difference with one another, which is predictable according to the definition of molecular total energy. As for stereoisomers, the total energies of compounds in groups (a) or (d) are greater than those of the corresponding compounds in groups (c) or (b); that is, the compounds in groups (a) or (d) are less stable than corresponding compounds in groups (c) or (b), and this is possibly caused by the difference in the π -conjugation effect. In addition, the energy differences between stereoisomers are equal to or less than $20 \text{ kJ}\cdot\text{mol}^{-1}$ except for two groups of stereoisomers (namely, A-a and A-c, B-3a and B-3c), which also points toward the possibility of the existence of the stereoisomers.

According to the optimized parameters (listed in Tables 2 and 3), the bond lengths of N7–N7' are around 1.255 \AA ,

slightly longer than a typical N=N bond (1.252 \AA) [61]. Also, all bonds formed by other C or N atoms are shorter than their typical single bond (1.450 \AA) counterparts and longer than their typical double bond (1.270 \AA) counterparts [61]. Furthermore, the same trend exists in each group of those bonds in the rings, in that they become more homogeneous when nitrogen content increases. Finally, for all the compounds (with C-45d as an exception), the $\text{H}_2\text{N-C}$ bond or N-(N=N) bond (corresponding to the N-NH₂ of the reactant molecules) is never the longest bond, which is quite different from the condition in 1,5-diaminotetrazole, because in this molecule, the N-NH₂ (1.383 \AA) is the longest [62]. This should result from the π conjugation between the N=N and the five-membered ring.

The bond angles of these optimized structures prove that all the atoms in the five-membered ring have a sp^2 hybridization. In 1,5-diaminotetrazole, the values of N=N-NH₂ and C-N-NH₂ are quite close (125.13° and 126.02° , respectively) [62], while this phenomenon is absent in 5,5'-bis(amino)-1,1'-azobis(tetrazoles). The bond angle of

Table 2 Optimized structural parameters of the compounds in group (a) and (b) calculated at B3LYP/6-31++g(d, p) level

Bond	A-a	B-3a	B-4a	B-5a	C-34a	C-35a	C-45a	D-345a
N1–C2	1.390	1.369	1.388	1.371	1.367	1.351	1.366	1.346
C2–X3	1.378	1.311	1.374	1.385	1.310	1.321	1.384	1.322
C2–N6	1.404	1.403	1.405	1.393	1.400	1.391	1.384	1.380
X3–X4	1.435	1.390	1.389	1.418	1.397	1.370	1.369	1.368
X4–X5	1.365	1.359	1.300	1.322	1.295	1.315	1.286	1.276
X5–N6	1.402	1.405	1.396	1.377	1.394	1.380	1.394	1.386
N6–N7	1.361	1.361	1.362	1.356	1.362	1.355	1.355	1.355
N7–N7'	1.257	1.258	1.254	1.257	1.254	1.259	1.255	1.256
C2–N6–N7	131.67	132.77	132.72	132.14	133.81	133.17	133.30	134.42
C5–N6–N7	118.80	120.62	120.19	115.08	121.90	117.12	115.72	117.56
N6–N7–N7'	114.26	114.05	113.71	113.93	113.45	113.24	113.39	112.72
N1–C2–X3–X4	−171.24	−174.67	−171.07	−175.81	−174.19	−178.25	−176.02	−178.29
X5–N6–N7–N7'	167.04	172.44	167.02	175.37	171.19	177.41	175.54	177.22
N6–N7–N7'–N6'	178.01	178.33	178.19	179.75	178.12	179.28	179.6	179.21
Bond	A-b	B-3b	B-4b	B-5b	C-34b	C-35b	C-45b	D-345b
N1–C2	1.399	1.384	1.384	1.395	1.367	1.378	1.379	1.360
C2–X3	1.381	1.331	1.379	1.380	1.329	1.330	1.378	1.327
C2–X4	1.439	1.432	1.387	1.430	1.380	1.428	1.380	1.380
X3–N6	1.394	1.366	1.398	1.382	1.372	1.353	1.377	1.350
X4–X5	1.372	1.373	1.310	1.326	1.313	1.325	1.296	1.296
X5–N6	1.380	1.368	1.373	1.350	1.362	1.337	1.354	1.342
N6–N7	1.361	1.359	1.361	1.360	1.358	1.360	1.360	1.359
N7–N7'	1.259	1.254	1.259	1.257	1.254	1.254	1.256	1.253
C3–N6–N7	129.70	126.12	131.09	130.05	127.33	126.52	131.55	127.90
C5–N6–N7	120.13	120.85	121.07	116.58	122.15	117.37	116.49	117.60
N6–N7–N7'	112.55	112.95	112.10	111.85	112.60	112.04	111.43	111.63
N1–C2–X4–X5	176.45	176.66	177.15	176.42	177.46	176.60	177.09	177.62
X5–N6–N7–N7'	179.88	179.42	179.82	−179.67	179.89	179.84	−179.66	−179.76
N6–N7–N7'–N6'	179.95	179.89	179.89	−179.94	−180.00	179.96	179.96	−179.99

Bond lengths are in (\AA), bond angles are and dihedral angles are in ($^\circ$)

Table 3 Optimized structural parameters of the compounds in group (c) and (d) calculated at B3LYP/6-31++g(d, p) level

Bond	A-c	B-3c	B-4c	B-5c	C-34c	C-35c	C-45c	D-345c
N1–C2	1.389	1.371	1.386	1.374	1.367	1.355	1.367	1.348
C2–X3	1.376	1.311	1.372	1.384	1.309	1.322	1.382	1.322
C2–N6	1.395	1.390	1.396	1.382	1.389	1.377	1.375	1.369
X3–X4	1.437	1.391	1.390	1.420	1.398	1.371	1.370	1.369
X4–X5	1.369	1.364	1.302	1.327	1.298	1.319	1.291	1.280
X5–N6	1.402	1.406	1.401	1.373	1.398	1.381	1.393	1.390
N6–N7	1.359	1.358	1.362	1.356	1.361	1.354	1.357	1.355
N7–N7'	1.255	1.257	1.252	1.251	1.253	1.252	1.249	1.250
C2–N6–N7	119.83	121.34	120.90	119.97	122.47	121.77	121.01	122.93
C5–N6–N7	130.16	131.50	131.72	126.63	132.89	127.98	127.59	128.73
N6–N7–N7'	113.25	112.85	113.02	113.63	112.71	113.36	113.29	113.90
N1–C2–X3–X4	–175.77	–176.44	–174.99	–176.28	–175.94	–177.53	–176.51	–177.88
X5–N6–N7–N7'	–0.92	–0.54	–1.55	–3.29	–0.45	–2.95	–4.46	–3.50
N6–N7–N7'–N6'	–179.94	–179.71	179.93	179.00	–179.65	179.61	178.75	179.71
Bond	A-d	B-3d	B-4d	B-5d	C-34d	C-35d	C-45d	D-345d
N1–C2	1.404	1.387	1.390	1.400	1.364	1.382	1.385	1.371
C2–X3	1.376	1.326	1.373	1.378	1.324	1.327	1.375	1.324
C2–X4	1.438	1.433	1.386	1.428	1.379	1.427	1.376	1.381
X3–N6	1.396	1.367	1.400	1.381	1.349	1.353	1.376	1.372
X4–X5	1.375	1.373	1.312	1.330	1.298	1.326	1.302	1.313
X5–N6	1.382	1.372	1.378	1.349	1.345	1.338	1.355	1.369
N6–N7	1.362	1.359	1.365	1.364	1.365	1.362	1.368	1.361
N7–N7'	1.256	1.256	1.254	1.250	1.250	1.252	1.248	1.255
C3–N6–N7	120.03	116.58	121.35	120.47	117.69	117.10	121.62	118.20
C5–N6–N7	129.89	130.47	131.00	126.18	131.95	126.83	126.49	127.43
N6–N7–N7'	112.99	112.23	112.77	113.13	112.00	112.30	112.76	112.01
N1–C2–X4–X5	176.27	176.38	176.98	176.35	177.28	–176.40	176.85	–177.38
X5–N6–N7–N7'	–0.49	–0.94	0.60	–0.40	–0.24	1.39	2.64	0.03
N6–N7–N7'–N6'	180.00	179.97	180.00	–180.00	180.00	–180.00	180.00	–180.00

Bond lengths are in (Å), bond angles are and dihedral angles are in (°)

N–N–(N=N) becomes bigger and that of C–N–NH₂ becomes smaller, but the sum of them changes little, which suggests that this alteration is mainly caused by the rotation of the five-membered rings in their molecule planes. In groups (a) and (b), C2–N6–N7 (C3–N6–N7 for the molecules in group (b)) are bigger than C5–N6–N7, and this relationship is reversed for molecules in groups (c) and (d); both changes may be attributed to the lone pair electronic repulsion between N atoms of the N–N=N–N structure and the NH₂-five-membered ring. In addition, the electron repulsion between nitrogen atoms of N–N=N–N structure may be a response to N6–N7–N7' being smaller than 120°.

N1–C2–X3–X4 (N1–C2–X4–X5 for groups (b) and (d)), X5–N6–N7–N7', and N6–N7–N7'–N6' can reflect the angles formed by azoles –NH₂, azoles –(N=N) and azoles–azoles to some extent. Hence, their values show that all the C atoms and N atoms of each compound almost stay in one plane. Together with the values of the bond length, the π conjugation bond is thought to exist on the whole molecular plane. Compounds in group (c) have more planar structures than their

corresponding stereoisomers in group (a), which may explain why compounds in group (c) have lower total energies than their corresponding stereoisomers. As for compounds in groups (b) and (d), they have even dihedral angles with their stereoisomers, that is, C and N atoms of each compound in both group form perfect planes, while in group (d), atoms supplying lone electrons are more dispersed, thus, weaker π bonds and lower stability structures may be the result.

Natural bond analyses

Net charge distribution

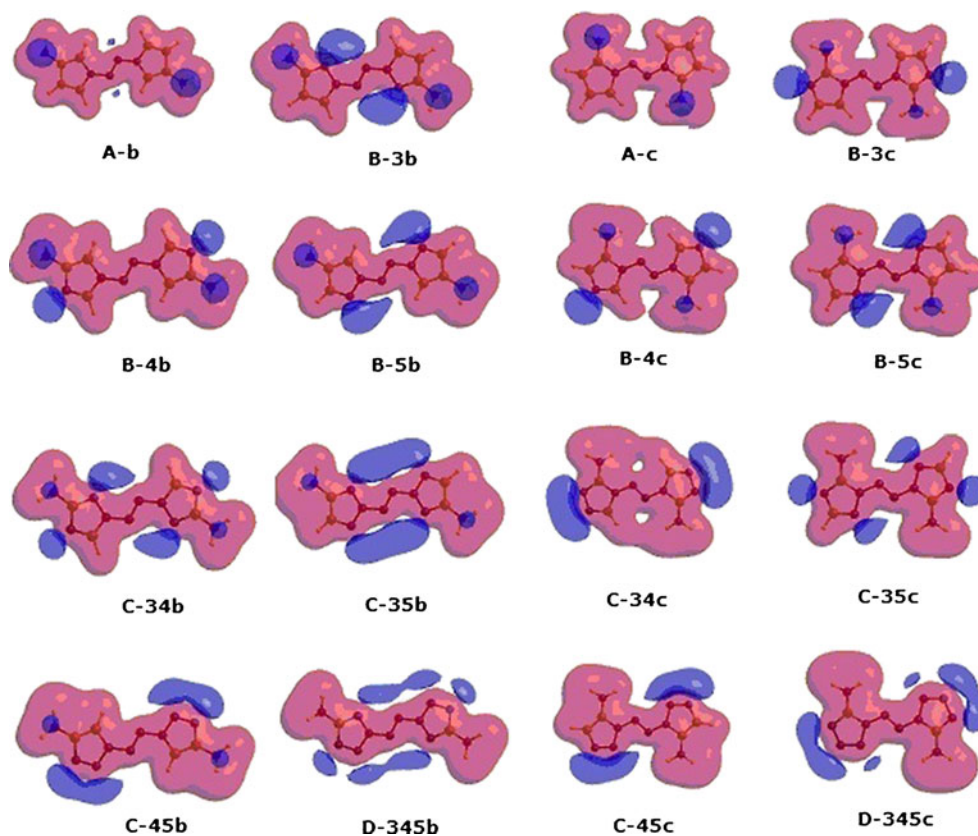
The net charge distribution of the optimized structures was obtained using a natural bond orbital (NBO) analysis. Results show that the net charge distribution of each compound is close to that of its stereoisomer, therefore, only the net charges of non-hydrogen atoms of compounds in groups (b) and (c) are listed in Table 4 for comparison.

Table 4 The calculated natural atomic charges (e) of compounds in group (b) and (c) at B3LYP/6-31++G(d, p) level

atoms	Natural charge							
	A-b	B-3b	B-4b	B-5b	C-34b	C-35b	C-45b	D-345b
N1	-0.9	-0.9	-0.9	-0.8	-0.8	-0.8	-0.8	-0.8
C2	0.1	0.3	0.3	0.1	0.5	0.3	0.3	0.5
X3	-0.2	-0.4	-0.2	-0.1	-0.4	-0.3	-0.2	-0.3
X4	0.0	-0.4	-0.5	-0.1	-0.5	-0.1	-0.3	-0.3
X5	0.0	0.3	0.2	-0.3	0.2	-0.2	0.0	0.0
N6	-0.2	-0.1	-0.2	0.0	-0.1	0.1	0.0	0.1
N7	-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0
	A-c	B-3c	B-4c	B-5c	C-34c	C-35c	C-45c	D-345c
N1	-0.9	-0.8	-0.9	-0.8	-0.8	-0.8	-0.8	-0.8
C2	0.3	0.6	0.3	0.4	0.5	0.6	0.3	0.6
X3	-0.4	-0.6	-0.2	-0.4	-0.4	-0.6	-0.2	-0.4
X4	-0.3	-0.1	-0.4	0.0	-0.3	0.2	-0.2	0.0
X5	-0.1	-0.2	0.1	-0.3	0.10	-0.3	-0.1	-0.1
N6	-0.2	-0.3	-0.3	-0.1	-0.3	-0.1	-0.1	-0.1
N7	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

From Table 4, we can see that N atoms of the $-NH_2$ group have the most negative natural charge for every compound. The C atoms adjacent to them always carry the

most positive natural charge. Meanwhile, with the increase in the number of nitrogen atoms in the five-membered ring, the N1 atom carries less and less negative charge; that is, more N atoms in the ring leads to more negative charge transferring from the $-NH_2$ to the five-membered ring. The charges of C2 are greatly influenced by its surrounding atoms. If the other two atoms bonded with it are N atoms (in C-34b, D-345b, B-3c, C-34c, C-35c, D-345c), the positive charge carried by C2 is the most (about 0.5e), and if the other two atoms bonded with it are C atoms, it will carry less positive charge (in A-b, B-5b), which is attributed to the lower electronegativity of C atoms than N atoms. Owing to the inductive effect of $-NH_2$, the other two atoms bonded with C2 carry negative charge whether they are C or N atoms; for compounds in group (b), they are X3 and X4, for compounds in group (c), they are N6 and X3. For the other atoms in the five-membered ring, their charges are determined by the inductive effect of $-NH_2$, themselves and their surroundings. For example, for N6 in group (b), if the atoms bonded with it in the ring are N atoms, it will carry a positive charge, whereas for N5 in group (c), if it itself is an C atom, and the no.4 atom (which is the only atom except N6 in the ring bonded with it) is N, it will carry positive charge, otherwise it will carry negative charge and this is thought to be due to the inductive effect of the $-NH_2$.

Fig. 4 The MESP surface for compounds of group (b) and (c) calculated at B3LYP/6-31++G(d, p) level with the isovalue of 1ev

Molecular electrostatic potential

The molecular electrostatic potential (MESP) of structures can be used to predict coordination sites successfully. With blue and red denoting negative and positive MESP, respectively, Fig. 4 shows the electrostatic map for the 16 structures of groups (b) and (c); the conditions are similar between stereoisomers. On the whole, positive MESP is mainly distributed in the inner of the molecules, while negative MESP, which is mostly attributed to the lone electron pair supplied by N atoms, is around the N atoms. Meanwhile, with the increase of N atoms in the azole rings, the negative area of $-\text{NH}_2$ becomes smaller, while that of the five-membered ring becomes wider, owing to the fact that N atoms in the rings contribute to the transfer of negative charge from $-\text{NH}_2$ to the rings. All of these findings agree well with the results of the analysis of net charge distribution.

Compared with compounds in group (c), compounds in group (b) have larger negative MESP areas around $\text{N}=\text{N}=\text{N}$ –N, which is especially demonstrated by C-35b, which was explained as follows. The longer distance between $-\text{NH}_2$ and $\text{N}=\text{N}=\text{N}$ –N in group (b) compounds compared to group (c) compounds means that the H (which carries a positive charge) on $-\text{NH}_2$ has a weaker shielding effect on $\text{N}=\text{N}=\text{N}$ –N. In C-35b and D-345b, no hydrogen atoms bond with the adjacent atoms of $\text{N}=\text{N}=\text{N}$ –N and thus the negative MESP around them is wider and linked together.

Based on the above analysis, the conclusion may be reached that the N atoms of the five-membered ring and $-\text{NH}_2$ may coordinate with other cations. Meanwhile, with the increase in nitrogen content, the N atom of the five-membered ring is more able than the N in $-\text{NH}_2$ to supply lone electron pairs to centrally coordinated atoms. Although nitrogen atoms in $\text{N}=\text{N}=\text{N}$ –N structure mostly take negative charge and sometimes the negative MESP around them are wide, our suggestion is that they have less chance to become coordinate atoms because of the steric crowding.

Thermal stability

Bond dissociation energy is a useful index to evaluate the thermal stability of the studied compounds. Generally, the smaller the BDE of a bond, the easier it becomes a trigger bond in reaction. Meanwhile, compounds with the lowest BDE possibly have the highest chemical reactivity. For the title compounds, the out-ring C–N bonds are the relative weak bonds in the molecules. Hence, calculated values of BDEs of these bonds are listed in Table 5 to study the relative thermal stabilities.

As is shown in the table, BDE of C6–N7 is much smaller than that of N1–C2 for each compound. For C2–N1 bonds, bond dissociation energies among stereoisomers are quite

Table 5 Bond dissociation energies (BDE, $\text{kJ}\cdot\text{mol}^{-1}$) for the title compounds at B3LYP/6-31++g(d, p) Level

Compounds	BDE	
	N1–C2	N6–N7
A-a	455.30	83.76
A-b	450.81	131.11
A-c	466.02	95.05
A-d	449.40	123.27
B-3a	470.61	90.66
B-3b	464.36	163.05
B-3c	477.70	103.18
B-3d	466.29	162.33
B-4a	457.02	84.30
B-4b	464.15	117.31
B-4c	465.08	87.10
B-4d	461.19	99.94
B-5a	481.39	160.47
B-5b	454.49	166.41
B-5c	474.67	154.94
B-5d	452.47	154.19
C-34a	480.84	103.56
C-34b	489.15	157.41
C-34c	486.96	107.69
C-34d	489.81	147.59
C-35a	497.88	160.09
C-35b	474.15	161.89
C-35c	500.22	162.79
C-35d	474.78	155.41
C-45a	483.62	145.14
C-45b	475.28	150.92
C-45c	488.59	141.63
C-45d	471.95	130.85
D-345a	510.72	156.05
D-345b	503.50	158.11
D-345c	512.99	153.18
D-345d	502.74	142.65

close, with a difference less than $12\text{ kJ}\cdot\text{mol}^{-1}$. Compounds with the same molecule formulation are slightly different from each other. That is, for compounds in set A, BDEs of C2–N1 range from $449.40\sim 466.02\text{ kJ}\cdot\text{mol}^{-1}$, in set B, $452.47\sim 481.39\text{ kJ}\cdot\text{mol}^{-1}$, in set C, $471.95\sim 500.22\text{ kJ}\cdot\text{mol}^{-1}$, in set D, $502.74\sim 512.99\text{ kJ}\cdot\text{mol}^{-1}$. The bond dissociate energy of N1–C2 roughly increases with the nitrogen content in the molecules. The condition of C6–N7 bonds is not the same. The margin of BDEs between stereoisomers differs from $2\text{ kJ}\cdot\text{mol}^{-1}$ to $20\text{ kJ}\cdot\text{mol}^{-1}$, and BDEs of isomers are quite different with each other. Besides, the strength of C6–N7 does not relate much with the number of nitrogen atoms in the ring, however, the atoms adjacent with C6 are dominant factors. If the adjacent atom is N, the BDE of C6–N7 for the corresponding compound is relatively strong.

For example, BDE of B-5a are much bigger than those of B-3a, B-4a and C-34a; BDE of B-4b are much smaller than those of B-3b, B-5b, C-35b, C-34b, C-45b and D-345b. This may be caused by the inductive effect of N atoms.

Based on the above analyses, we can come to the conclusion that all of the studied compounds may decompose with the rupture of the two azole rings, and for different molecules, N atom in meta-position of the linked C atom may improve the thermal stability of the compounds.

Frontier orbital energy levels and their gaps

Frontier orbital energy levels are very useful in predicting reactive properties. Together with the total energies, the highest occupied molecular orbital energies (E_{HOMO}) and the lowest unoccupied molecular orbital energies (E_{LUMO}) and their gaps ($E_{\text{L-H}}$) are listed in Table 1.

There is a rough trend that the E_{LUMO} and E_{HOMO} decrease with the increase in nitrogen content. The E_{LUMO} of compound D-345a, which has the highest nitrogen content, is the lowest in all the title compounds, and so is its E_{HOMO} . The result is that values of $E_{\text{L-H}}$ are relatively more concentrated even though the range of E_{LUMO} and E_{HOMO} is wide. Hence, for all bis(amino)-azobis(azoles), the nitrogen content predominantly influences E_{LUMO} and E_{HOMO} , while $E_{\text{L-H}}$ does not change much with it. For molecules in series B and D of groups (a) and (c), compounds with the longest nitrogen chain have the biggest $E_{\text{L-H}}$, for example, $E_{\text{L-H}}$ of B-5a is larger than that of B-4a and B-3a. However, a similar trend is not found in groups (b) and (d), and $E_{\text{L-H}}$ of C-45b is the smallest in series C of group (b). Thus, for isomers, the nitrogen chain does not influence $E_{\text{L-H}}$ in this way.

The difference between stereoisomers is not much, mostly about $10 \text{ kJ}\cdot\text{mol}^{-1}$ or so, and some regular patterns can be found as well. Except for B-5b ($E_{\text{L-H}}=336.35 \text{ kJ}\cdot\text{mol}^{-1}$) and its stereoisomer B-5d ($E_{\text{L-H}}=342.93 \text{ kJ}\cdot\text{mol}^{-1}$), the $E_{\text{L-H}}$ of all the compounds in group (b) is greater than that of their corresponding stereoisomers in group (d). This result is consistent with the total energies, that is, both lead to greater stability. Whereas all compounds in group (a) apart from B-5a ($E_{\text{L-H}}=368.32 \text{ kJ}\cdot\text{mol}^{-1}$, its stereoisomer B-5c, $E_{\text{L-H}}=375.04 \text{ kJ}\cdot\text{mol}^{-1}$) and C-35a ($E_{\text{L-H}}=376.64 \text{ kJ}\cdot\text{mol}^{-1}$, its stereoisomer C-35c, $E_{\text{L-H}}=384.69 \text{ kJ}\cdot\text{mol}^{-1}$) are more chemically stable than their corresponding stereoisomers in group (c), while compounds in the latter group may more stably exist than compounds in the former group.

Of all the studied compounds, D-345a has the biggest $E_{\text{L-H}}$ ($388.20 \text{ kJ}\cdot\text{mol}^{-1}$), followed by D-345c, C-35c and C-35a; meanwhile, B-4d has the smallest $E_{\text{L-H}}$ ($291.47 \text{ kJ}\cdot\text{mol}^{-1}$). Thus, it may be inferred that D-345a is the most chemically stable, and B-4d is the most reactive.

Heats of formation and densities

Because the title compounds have no oxygen atoms in their molecules, that is, H and C cannot combust into their oxide compounds, therefore the heat of formation is the sole source of detonation heat for these compounds. Together with the K-J equation, we can see that there is a linear relationship between the explosive velocity and $(\Delta_f H)^{1/4}$, the explosive pressure and $(\Delta_f H)^{1/2}$, and that all these suggest HOF to be quite an important parameter in determining the explosive properties for the investigated compound. Density is another important parameter for energetic compounds; the K-J equation shows that explosive velocity increases linearly with density and explosive pressure increases linearly with the square of density. Therefore, we compared HOFs and densities of the title compounds in Table 6 and investigated the effects of nitrogen content and nitrogen chain on them.

It is evident from the results of calculated HOFs that all the compounds have high positive heats of formation, and even the smallest of them is as high as $813.5 \text{ kJ}\cdot\text{mol}^{-1}$. A general trend exists in each group whereby the HOFs increase with the nitrogen contents. Compounds of serial D (Fig. 2) always have the highest HOFs when compared with the other compounds in their groups. The difference in HOFs between stereoisomers is small, just like the case for $E_{\text{L-H}}$ and total energy. Furthermore, exactly as is the case for the total energy, the HOFs of compounds in group (a) are higher than those of their corresponding stereoisomers, and the HOFs of compounds in group (b) are lower than those of their corresponding stereoisomers. This implies that for stereoisomers, the more stable the structure is, the lower the HOF it has. Differences between isomers are also worthy of discussion, as heats of formation of compounds with the same molecular formulas show significant deviations. Compared with D-345b, which has an N8 chain, D-345c (with an N10 chain) has a bigger HOF; the HOF of B-3b (with an N6 chain) is higher than that of B-3c (with an N4 chain); in each group, B-5a (or B-5b, B-5c, B-5d) has the biggest HOF of the same serial. The HOF of C-45a is close to that of D-345c, but that of another structure in its serial (C-35a) is even smaller than A-a's, the difference in the relative positions of atoms is responsible for almost $200 \text{ kJ}\cdot\text{mol}^{-1}$ difference between their HOFs. Furthermore, in each group, the compounds with the longest nitrogen chain always have the highest heat of formation, which may be attributed to their N–N bonds.

In order to more rigorously discuss the effect of the nitrogen content and nitrogen chain on the HOFs of bis(amino)-azobis(azoles), we reproduced the data for A-c, B-5c, C-45c and D-345c in Fig. 5a and obtained the following expression: $\text{HOF}=688.34+42.735n$; $R=0.98182$, where n denotes the number of nitrogen atoms in the N chain, and R denotes the coefficient. It can be seen from the expression that in bis

Table 6 Predicted HOFs ($\text{kJ}\cdot\text{mol}^{-1}$), molar volume ($\text{cm}^3\cdot\text{mol}^{-1}$), ρ ($\text{g}\cdot\text{cm}^{-3}$), D ($\text{m}\cdot\text{s}^{-1}$), P (GPa) and Q ($\text{cal}\cdot\text{g}^{-1}$) of the compounds

Compounds	HOFs	V	ρ	D	P	Q
A-a	884.3	129.52	1.47	6.44	16.16	1111.2
B-3a	828.2	117.74	1.63	7.17	21.49	1029.9
B-4a	880.1	112.70	1.71	7.50	24.18	1094.4
B-5a	928.2	115.83	1.66	7.46	23.51	1154.3
C-34a	955.6	108.25	1.79	8.27	30.27	1176.3
C-35a	860.6	110.05	1.76	7.96	27.80	1059.4
C-45a	1055.1	110.20	1.76	8.37	30.69	1298.7
D-345a	1108.6	108.37	1.81	8.93	35.48	1350.9
A-b	870.3	121.00	1.57	6.71	18.37	1093.5
B-3b	905.4	117.40	1.64	7.35	22.60	1126.0
B-4b	827.2	120.58	1.59	7.06	20.48	1028.7
B-5b	953.5	122.79	1.57	7.22	21.20	1185.8
C-34b	859.4	115.04	1.69	7.72	25.42	1057.8
C-35b	1010.6	122.02	1.59	7.72	24.50	1244.0
C-45b	1043.5	120.48	1.61	7.85	25.54	1284.5
D-345b	1095.3	108.91	1.80	8.87	34.93	1334.7
A-c	868.3	114.20	1.67	6.98	20.60	1091.1
B-3c	813.5	120.21	1.60	7.04	20.43	1011.6
B-4c	876.3	124.73	1.54	7.00	19.70	1089.8
B-5c	919.3	121.41	1.58	7.21	21.29	1143.2
C-34c	950.6	114.92	1.69	7.92	26.79	1170.1
C-35c	855.2	111.29	1.74	7.89	27.10	1052.7
C-45c	1054.3	118.74	1.64	7.95	26.43	1297.8
D-345c	1108.2	108.53	1.81	8.92	35.37	1350.3
A-d	882.5	121.08	1.57	6.73	18.47	1108.9
B-3d	912.1	121.47	1.58	7.19	21.19	1134.3
B-4d	851.2	118.81	1.62	7.18	21.39	1058.6
B-5d	999.7	113.89	1.69	7.69	25.23	1243.2
C-34d	877.6	108.29	1.79	8.09	28.99	1080.2
C-35d	1020.3	113.08	1.72	8.15	28.66	1256.0
C-45d	1064.7	111.16	1.75	8.34	30.30	1310.6
D-345d	1112.1	110.62	1.77	8.81	34.11	1355.1

(amino)-azobis(azoles), the heat of formation may increase by about $42.735 \text{ kJ}\cdot\text{mol}^{-1}$ when one $-\text{CH}-$ on the five-membered ring is displaced by $-\text{N}-$ and the nitrogen chain becomes longer.

The results of the calculated densities show that the title compounds do not have large densities. The largest of them is $1.81 \text{ g}\cdot\text{cm}^{-3}$, which is comparative with the experimental density of RDX. Since the molar masses of these compounds are quite close, molar volume is the decisive factor in their deviations in densities. In group (a), with the increase in nitrogen content, the molar volumes of the compounds decrease and their densities increase, and the difference among isomers is not great, but the case changed in other groups. In group (b), the molar volumes and densities

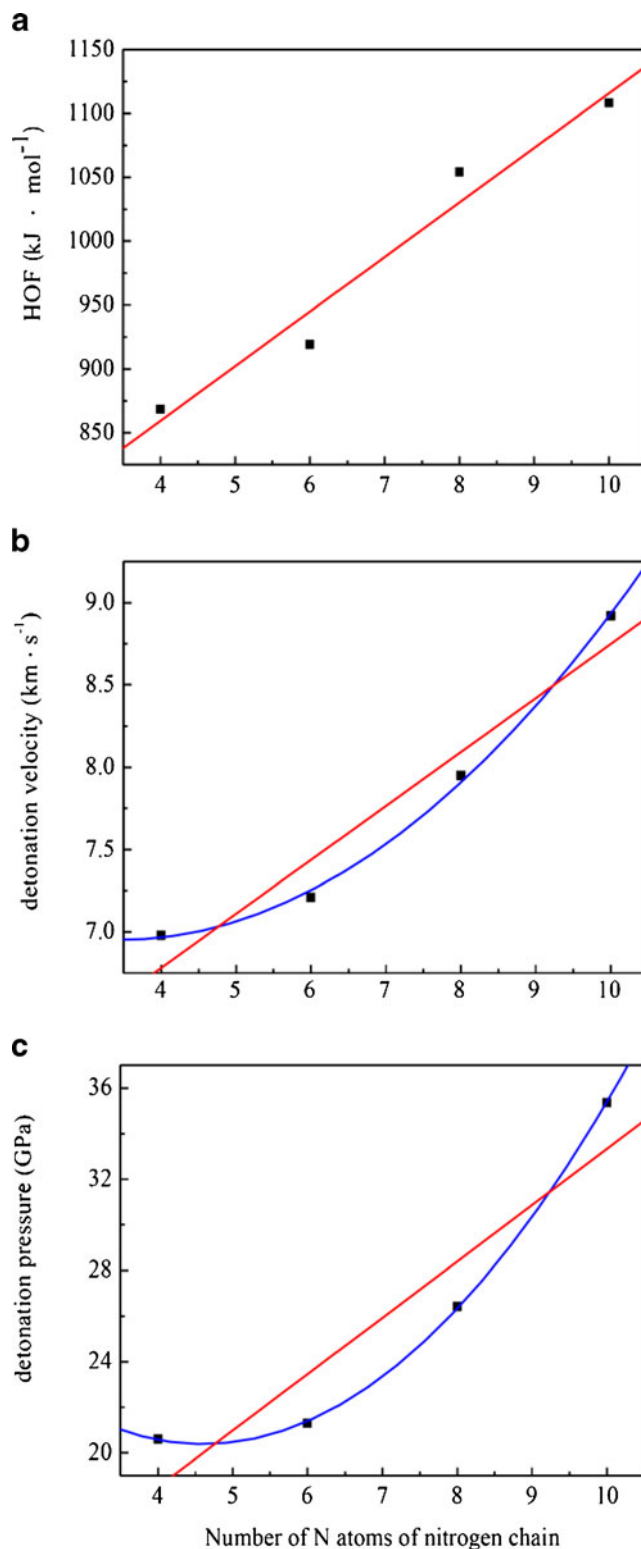


Fig. 5 The relationship between nitrogen chain and heats of formation, detonation velocities and detonation pressure

of serials A, B and C were close and the density of D-345b is the highest. In group (d), compounds of the latter two serials have similar densities and volumes. While in group

(c), the situation is quite different, A-c is denser than compounds in serial B, and denser when compared with compounds in serial C. In all groups, compounds in serial D consistently have relatively larger density, which may to some extent be attributed to their shorter bond lengths than other compounds.

Energetic properties

Explosive parameters, including detonation heat, detonation velocity and detonation pressure, are listed in Table 6. As mentioned before, the HOF is the sole source of detonation heat for these compounds and their molar masses are very close; thus, their detonation heats are in the same order as their HOFs. For compounds with the same molecular formula, the HOF and density are the only two factors influencing their energetic parameters, because their *N* and *M* values are the same. Compounds with higher HOFs (or higher detonation heat) and density are certain to perform better as energetic compounds. Mostly, both these factors are influential, because the difference in HOFs among isomers may be large and their density is always vital for energetic compounds. Comparing C-45a with C-34a, the former has a bigger HOF but smaller density, and has better explosive parameters. B-4a is denser but has a lower HOF than B-5a, and the evolution patent of their energetic performance is the same as density. For stereoisomers, as discussed before, their HOFs are close, hence the differences in their detonation velocity and pressure are more determined by their densities.

When $-\text{CH}-$ on the five-membered ring is displaced by $-\text{N}-$, the moles of gaseous detonation products of one molecule do not change and molar mass changes little, and the average molecular weight of gaseous products increases, thus *N* values of the investigated explosives are almost the same while *M* values increase with the nitrogen content. On the whole, for compounds with different nitrogen content, nitrogen content plays a vital role in improving explosive properties, because compounds with higher nitrogen content have larger density, detonation heat, and average molecular weight of gaseous products. For example, compared with A-c, B-3c has a lower HOF and density, while its detonation velocity and pressure are bigger than the former's, owing to its larger *M* arising from its higher nitrogen content.

To better illustrate the relationship between the nitrogen content or length of the nitrogen chain, we chose the explosive parameters of A-c, B-5c, C-45c and D-345c from the table and reproduced the data in Fig. 5b, c. The parabolic and linear relationship fitted for them can be expressed as follows: detonation velocity $=7.504-0.3195n+0.04625n^2$, $R=0.99829$ or detonation velocity $=5.469+0.328n$, $R=0.9688$.

Detonation pressure $=31.3025-4.74625n+0.51563n^2$, $R=0.99985$ or detonation pressure $=8.615+2.4725n$, $R=0.93686$.

With greater density, detonation heat and the average molecular weight of gaseous products, compounds of serial D perform better than the compounds of serial A, B and C as energetic compounds, and they have more excellent explosive parameters than RDX. While due to their low density and negative oxygen balance, none of the compounds investigated have more attractive explosive properties than HMX. Considering the chemical and physical properties of the title compounds, we think that compounds of serial D may hold the promise of application as primary explosives and energetic coordination compounds.

Conclusions

In this study, 36 structures of all bis(amino)-azobis(azoles) were designed and their stable configurations were obtained. The investigation of their molecular geometries, electronic structures, heats of formation and explosive properties proved:

- (1) The two symmetrical trans-form structures are more stable than the other four stereoisomers. When the two $-\text{NH}_2$ groups of the bis(amino) azoles molecule, which form the bis(amino)-azobis(azoles) compound, substitute in the adjacent atoms of the five-membered ring, the C_1 trans-form structure is the most stable; otherwise the C_2 trans-form structure is the most stable. All the structures are quite close to planar configurations.
- (2) With the increase in the number of nitrogen atoms, the nitrogen atoms in the five-membered ring are more and more likely to be coordinated atoms than $\text{N1}(\text{N1}')$ and $\text{N7}(\text{N7}')$ when the compounds coordinate with cations. All of the studied compounds may start to decompose with the rupture of the two azole rings. N atom in meta-position of the linked C atom may contribute to the thermal stability of the compounds.
- (3) All the investigated compounds have relatively high HOFs. In general, HOF increases with the nitrogen content. Also, a good linear relationship was found between the HOF and nitrogen chain or nitrogen content for compounds in group (c): $\text{HOF}=688.34+42.735n$, $R=0.98182$. The differences between stereoisomers in values of HOF are small, and the more stable the structure is, the smaller the value of HOF. For isomers, the difference in HOFs cannot be ignored, and the compounds whose nitrogen atoms form the longest nitrogen chain have the biggest HOFs.
- (4) Generally, compounds with higher nitrogen content have better explosive properties. For stereoisomers,

compounds with bigger densities may possibly have greater explosive detonation and pressures. HOF and density are the two determinants of explosive properties. Compounds in serial D have better performance than RDX as energetic compounds and are promising candidates for use in prime explosives and energetic coordination compounds.

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