REGULAR ARTICLE

Density functional theoretical study of A series of pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; n = 1–3; q = +1, 0, −1, −2, and −3)

Qian Shu Li · Yan Zhang

Abstract The structure and the stability of pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; n = 1–3; q = +1, 0, −1, −2, and −3), as high energy-density materials (HEDMs), have been investigated at the B3LYP/6-311+G* level of theory. The natural bond orbital analysis shows that the charge transfer plays an important role when the $A_n(N_5)_{6-n}^q$ species are decomposed to $A_n(N_5)_{5-n}N_3^q$ and N_2. The more negative charges are transferred from the N_2 molecule after breaking the N_5 ring, the more stable the systems are with respect to the decomposition. Moreover, the conclusion can be drawn that $Al(N_5)_5^{2-}$ and $Al_2(N_5)_4^{2-}$ are predicted to be suitable as potential HEDMs.

Keywords Pentazolide compounds · Density functional theoretical study · $A_n(N_5)_{6-n}^q$

1 Introduction

The first synthesis of a covalent azide HN_3 was reported by Curtius more than 100 years ago [1]. The N_5^+ was made as a cation in bulk compounds in 1999 [2] and a metastable radical N_4 was observed in 2002 [3]. These experimental works have attracted considerable interest. In recent years, there are plentiful theoretical and experimental studies on polynitrogen and

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the hypothetical existence of nitrogen-rich compounds, which could be high energy-density materials (HEDMs) [2–14]. For example, Gagliardi and Pyykkö [5,6] have reported two new kinds of nitrogen-rich compounds containing transition metal atoms, $Sc(\eta^7\text{-}N_7)$ and $\eta^5\text{-}N_5^- - M\text{-}\eta^7\text{-}N_7^{3-}$ (M = Ti, Zr, Hf, and Th). They predicted that ScN_7 and N_5ThN_7 should be prepared. Nonmetal elements such as sulfur and phosphorus can also be central atoms for stabilizing a number of nitrogen clusters. Wang [11,12] has reported nitrogen-rich sulfides $S(N_4)_m$ (m = 1–3) and nitrogen-rich phosphorus $P(N_n)_m$ (n = 3, 4, m = 1–4) compounds as HEDMs. In addition, some new species with azido group have appeared in the literature [15–21]. For example, the astonishingly stable $Si(N_3)_6^{2-}$ anion has been reported at the recent experimental study by Filippou et al. [17]. Compounds $(P(N_3)_3, [P(N_3)_4]^+, [P(N_3)_5], [P(N_3)_6]^-)$ with linear N_3 units were prepared by Roesky [20].

The bare, gas-phase N_5^- anion was observed in mass spectra [10]. The accurate CCSD-(T)/aug-cc-PVTZ calculations showed that the N_5^- anion is a D_{5h} system, lying 14.3 kcal/mol above the $N_3^- + N_2$ with the transition state (TS) barrier for decomposition of 27.8 kcal/mol [22]. The N_5^- was predicted to have $t_{1/2} = 2.2$ days, while the half-life time for HN_5 is expected to be only about 10 min in methanol at 0°C [23]. So, the synthesis of molecules with a high number of pentazole units as the pentazolide species is an attractive but challenging way to prepare HEDMs. In previous reports, Nguyen et al. have proposed $(N_5)_2N-N(N_5)_2$ [7], $N(N_5)_3$ [22] and $N_5N = NN_5$ [24]. Several pentazolides of groups 6 and 13–15 were studied theoretically as possible HEDMs by Straka and Pyykkö [25]. Their study showed that the stability of these systems increases with the negative charge on them. The neutral and cationic pentazolides are less

stable and have lower TS barriers than anionic pentazo-lides. Based on the study of Straka and Pyykkö, we investigate a series of pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; $n = 1$–3; $q = +1, 0, -1,$ $-2,$ and -3) in this paper in order to explore potential HEDMs and the factors in stabilizing this kind of penta-zolide compounds. Structures, relative energies and TS barriers are predicted using density functional method.

2 Computational method

The geometries of pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; $n = 1$–3; $q = +1, 0, -1, -2,$ and -3) are optimized at the B3LYP/6-311+G* level of theory. The B3LYP method is a hybrid functional method based on the Becke's three-parameter nonlocal exchange functional [26] with the nonlocal correlation due to Lee et al. [27].

The 6-311+G* basis set is a standard split-valence tri-ple-ζ plus polarization basis set augmented with diffuse functions [28]. To characterize the stationary points and to determine the zero-point vibrational energy (ZPVE) corrections, harmonic vibrational frequency calculations are performed at the same level of theory. To confirm that a given transition structure connects reactants and products, the intrinsic reaction coordinate (IRC) calculations are also performed with the Gonzalez–Schlegel second-order algorithm [29]. To further explore the electronic structures of the potential compounds, the analysis of natural bond orbital (NBO) [30] is also performed in the present paper. All calculations is done with the Gaussian 03 program [31].

3 Results and discussion

3.1 Geometrical structures of pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; $n = 1$–3; $q = +1,$ 0, $-2,$ and -3)

The mononuclear species $Al(N_5)_5^{2-}$, $Si(N_5)_5^-$, $P(N_5)_5$ and $S(N_5)_5^+$, as well as the dinuclear species $B_2(N_5)_4^{2-}$, $Al_2(N_5)_4^{2-}$, $Si_2(N_5)_4^{2-}$ and $P_2(N_5)_4$, and the trinuclear species $Al_3(N_5)_3^{2-}$, $Si_3(N_5)_3^{3-}$ and $P_3(N_5)_3$, were found to be genuine minima with all real vibrational frequencies. The optimized structures are shown in Figs. 1, 2 and 3, respectively. The A–N and A–A bond lengths for the studied systems are listed in Table 1. From Fig. 1, all $A(N_5)_5^q$ species belong to the group of C_{2v} symmetry. However, the $A_2(N_5)_4^q$ pentazolides shown in Fig. 2 belong to the group of C_2 ($Al_2(N_5)_4^{2-}$ and

$Si_2(N_5)_4^{2-}$) or C_{2h} ($P_2(N_5)_4$) symmetry, and the $A_3(N_5)_3^q$ pentazolides shown in Fig. 3 belong to the group of C_2 ($Al_3(N_5)_3^{2-}$) or C_3 ($Si_3(N_5)_3^{3-}$ and $P_3(N_5)_3$) symmetry. Many other possible isomers of title compounds, such as $S_3(N_5)_3^-$, $B_3(N_5)_3$, and $C_3(N_5)_3^{3-}$ having C_3 symmetry or C_{2v} symmetry, and $S_2(N_5)_2$ having C_{2h} symmetry etc., are also checked and are all theoretically predicted to be unstable as higher-order saddle points.

From Table 1, the Al–N bond lengths are 2.015, 2.043 and 2.066 Å for the aluminum mono-, di-, and tri-nuclear species, (structures **1**, **6**, and **9**), respectively. They are slightly larger than the sum (1.18 + 0.75 = 1.93 Å) of the covalent radius of Al and N. The P–N bond lengths are 1.771, 1.790, and 1.774 Å for the phosphorus analogies $P(N_5)_5$, $P_2(N_5)_4$ and $P_3(N_5)_3$, (structures **3**, **8**, and **11**), respectively. They are smaller than the sum (1.06 + 0.75 = 1.81 Å) of the covalent radius of P and N. The Si–N bond lengths are 1.869, 1.974 and 2.010 Å for the silicon mono-, di-, and tri-nuclear species, (structures **2**, **7**, and **10**), respectively. The Si–N bond lengths in $Si(N_5)_5^-$ is very close to the sum (1.11 + 0.75 = 1.86 Å) of the covalent radius of Si and N. The B–N bond lengths in $B_2(N_5)_4^{2-}$ are 1.519 Å, smaller than the covalent radius sum 1.57 Å of B and N. Namely, all A–N bond orders are close to one. In addition, it is shown that the change for Si–N bond lengths among silicon systems is larger than those changes for Al—N and P–N bond lengths along with the number of pentazolide ligands.

From Table 1, the A–A bond lengths in trinuclear species are smaller appreciably than those in dinuclear species except the Si–Si bond length. The A–A bond lengths in most of title compounds are slightly larger than their covalent radius sum in this paper. Only B–B bond length (1.557 Å) in $B_2(N_5)_4^{2-}$ is smaller than its covalent radius sum (1.64 Å) and show a double B–B bond. The reason is that each boron atom has been sp^2 hybridized to connect with one p$_z$ atom orbital of the adjacent boron atom to form the B–B π bond.

3.2 Stability

To evaluate the kinetics stability of the studied systems, the TS for breaking the pentazole ring are determined on the basis of previous results of experimental and theoretical studies [10,23–25]. And the IRC calculations are performed to confirm that a given TS connects reactants (title compounds) and products(N_2 and azide). The calculated TS barriers are listed in Table 1. A few examples of TS structures are shown in Fig. 4.

The energies of the studied systems were calculated relative to the corresponding central atoms (B, Al, Si, P,
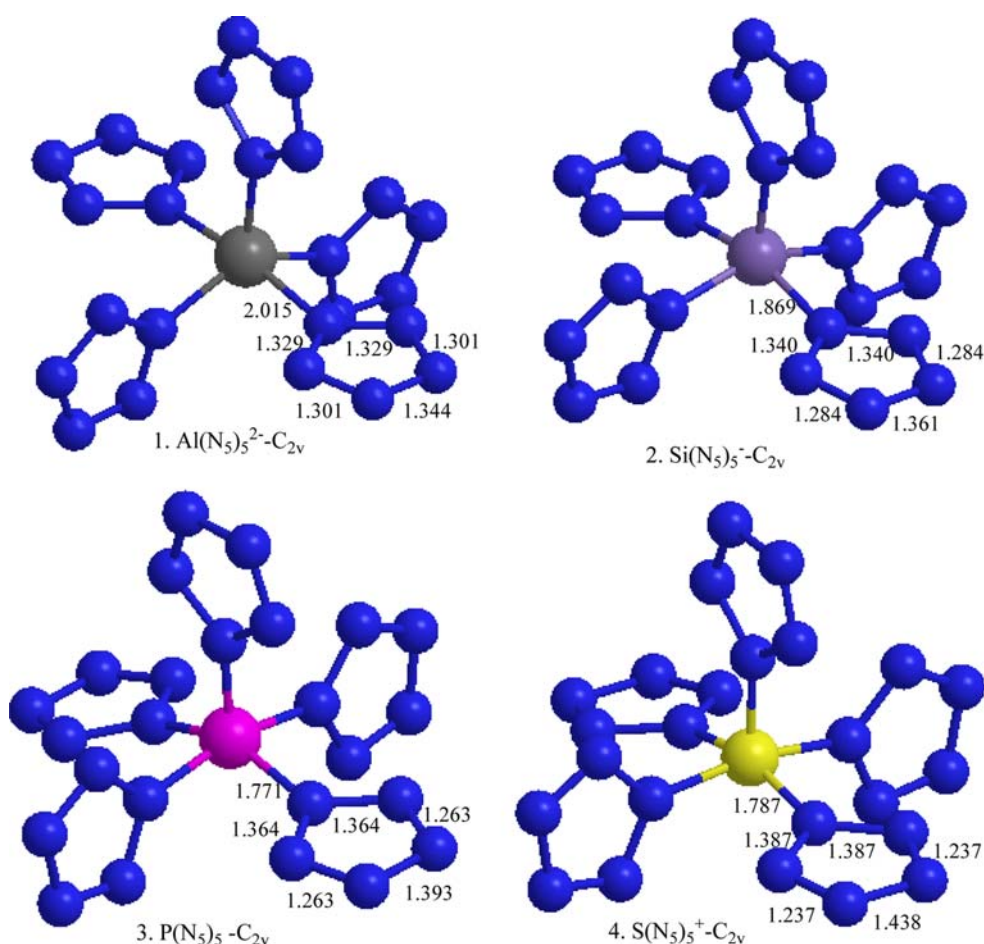
Fig. 1 Optimized structure of $A(N_5)_5$ (A = Al, Si, P, and S) pentazolides

and S) and N_2, as following:

$$A_n^q + \frac{5(6-n)}{2}N_2 \rightarrow A_n(N_5)_{6-n}^q$$
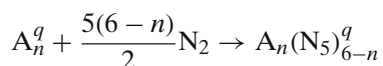
A zero-point vibrational correction was included in the calculation. To compare systems with a different amount of substituents, we use the "per N_2 unit" energies in the discussion. The relative energies (Table 1, all endothermic energy after zero-point energy correction) confirm the high energy content, and TS barrier of the substantial shows the kinetics stability towards $A_n(N_5)_{5-n}(N_3)^q$ and N_2 for the studied systems.

For all the mononuclear $A(N_5)_5^q$ pentazolides, the TS barriers increase with the decrease of relative energies. The relative energy of $Al(N_5)_5^{2-}$ lies even lowest in $A(N_5)_5^q$, but it has the highest TS barrier for decomposition of 18.5 kcal/mol. The relative energy of $S(N_5)_5^+$ lies highest in $A(N_5)_5^q$, but it has the lowest TS barrier for decomposition of 1.5 kcal/mol. It is also found that the kinetics stability of systems increases with negative charge on the system. The $Al(N_5)_5^{2-}$ has the

highest TS barrier and shows strongest stability, while the neutral compound $P(N_5)_5$ has a relatively lower TS barrier. And the $S(N_5)_5^+$ has the lowest TS barrier among $A(N_5)_5^q$ pentazolides. In addition, for the $A(N_5)_5^q$ (A=Al, Si, P, and S) species whose cental atoms are the third row elements in the Periodic Table, the kinetics stability decreases from the left to the right with the reduction of negative charges on the mononuclear pentazolides.

The dinuclear pentazolides (Fig. 2, Table 1), have a similar stability to the corresponding mononuclear pentazolides. Among them, $B_2(N_5)_4^{2-}$ and $Al_2(N_5)_4^{2-}$ possess significant kinetics stability because of their high TS barriers (19.2 kcal/mol) for decomposition. Their relative energies are 4.9 and 14.3 kcal/mol, respectively, showing $B_2(N_5)_4^{2-}$ is more stable than $Al_2(N_5)_4^{2-}$ due to strong B–N bond. And $Al_2(N_5)_4^{2-}$ is of higher energy content.

The trinuclear pentazolides, (Fig. 3, Table 1), behave differently from the mono-, di-nuclear pentazolides. (1) They lie even lower energetically than mono- and
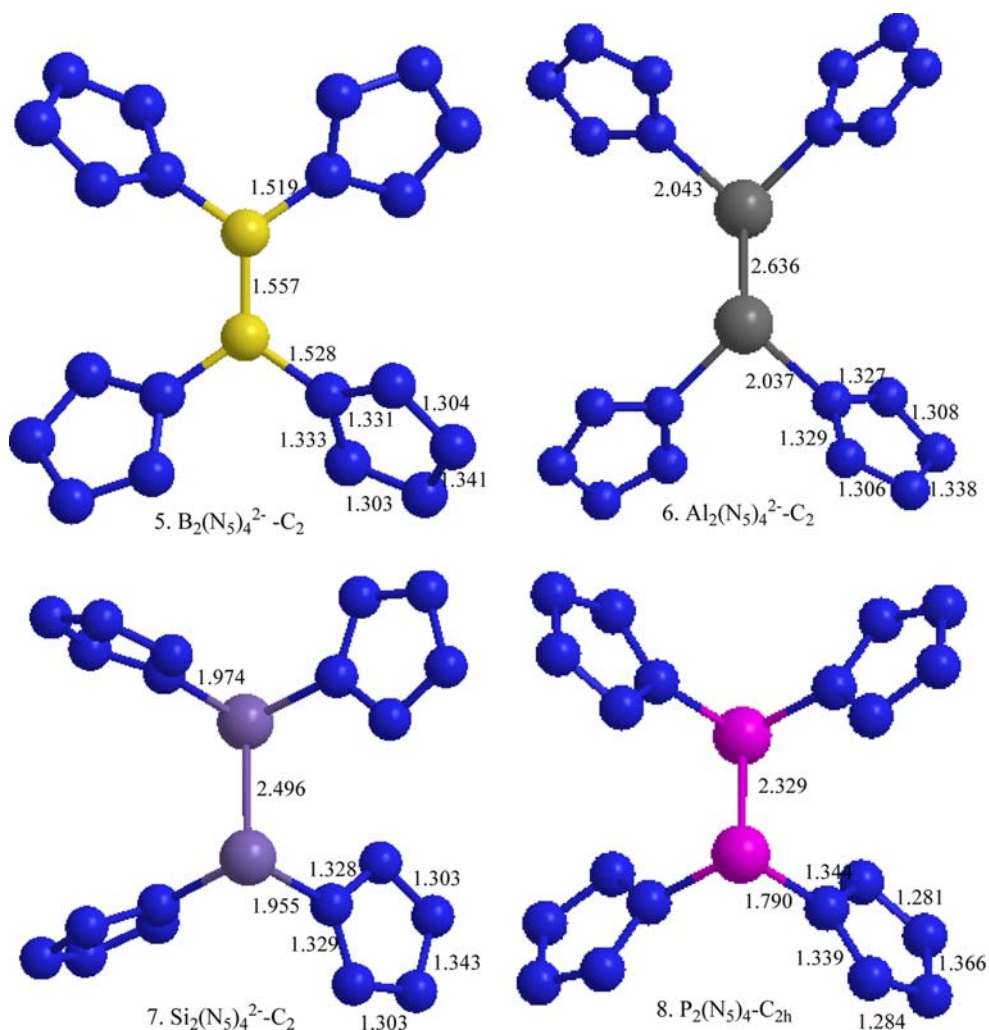
Fig. 2 Optimized structure of $A_2(N_5)_4$ (A = B, Al, Si, and P) pentazolides

Table 1 Calculated relative energies from Eq. 1 (ΔH), TS barriers (E_{ts}), A–N, A–A distances (Å) for the studied systems, and number of the transferred charges (N_{tc}) from the N_2 molecule after breaking the N_5 ring

| Structure	System	Symmetry	ΔH^a	E_{ts}^b	A–N	A–A	N_{tc}
1	$Al(N_5)_5^{2-}$	C_{2v}	13.5	18.5	2.015		−0.19
2	$Si(N_5)_5^-$	C_{2v}	25.2	12.3	1.869		−0.10
3	$P(N_5)_5$	C_{2v}	44.1	5.8	1.771		−0.02
4	$S(N_5)_5^+$	C_{2v}	50.3	1.5	1.787		0.06
5	$B_2(N_5)_4^{2-}$	C_2	4.9	19.2	1.519 1.528	1.557	−0.23
6	$Al_2(N_5)_4^{2-}$	C_2	14.3	19.2	2.043 2.037	2.636	−0.23
7	$Si_2(N_5)_4^{2-}$	C_2	20.4	18.5	1.974 1.955	2.496	−0.22
8	$P_2(N_5)_4$	C_{2h}	24.6	9.6	1.790	2.329	−0.08
9	$Al_3(N_5)_3^{3-}$	C_2	16.4	20.2	2.066 2.072	2.479	−0.25
10	$Si_3(N_5)_3^{3-}$	C_3	14.9	19.9	2.010	2.503	−0.30
11	$P_3(N_5)_3$	C_3	6.4	11.0	1.774	2.298	−0.10

[a] In kcal/mol per N_2 unit
[b] TS Barrier in kcal/mol for breaking the N_5 ring

di-nuclear pentazolides. (2) The TS barriers do not increase along with the decrease of relative energies. (3) The TS barriers (20.2 and 19.9 kcal/mol) for $Al_3(N_5)_3^{2-}$ and $Si_3(N_5)_3^{3-}$ with two and three negative charges are very close and higher than that (11.0 kcal/mol) of $P_3(N_5)_3$.
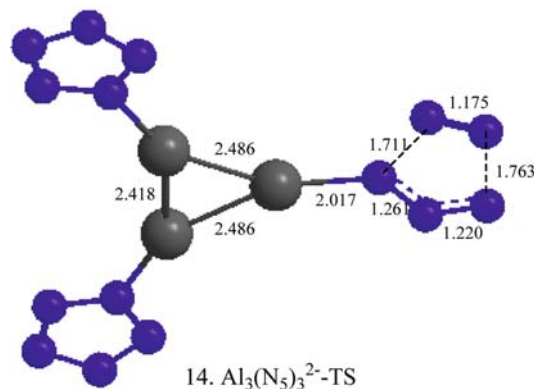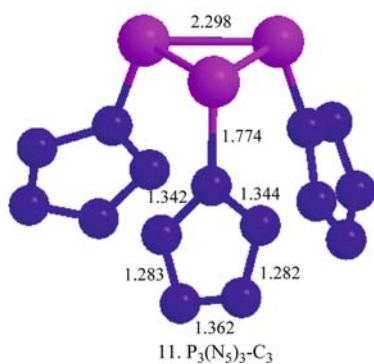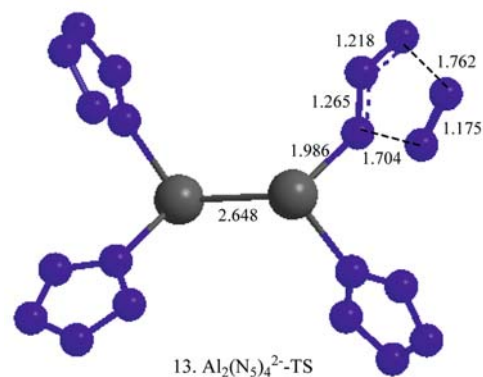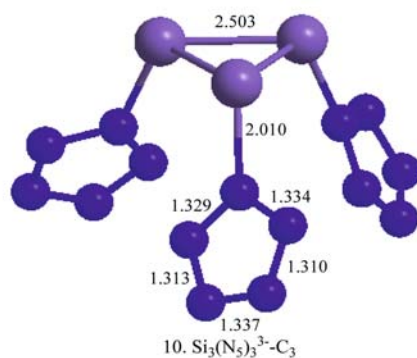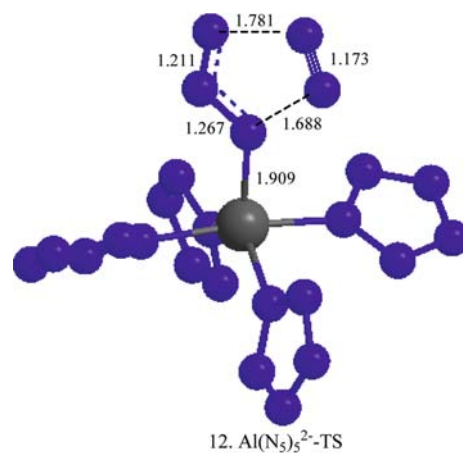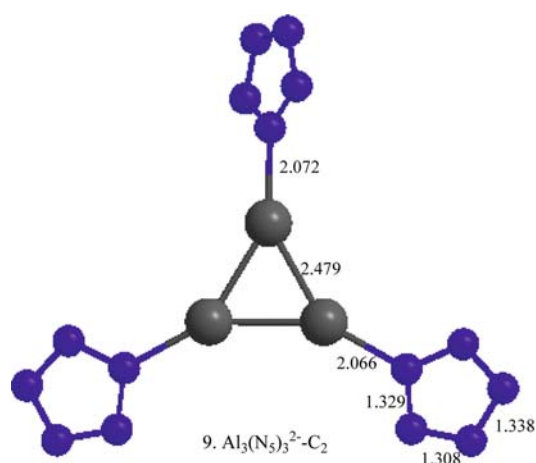
Fig. 3 Optimized structure of $A_3(N_5)_3$ (A = C, Al, Si, and P) pentazolides

Fig. 4 Selected transition states for pentazolides

In conclusion, the relative energies are decreased greatly along with the increase of the central element to-nitrogen ratio. For example, the relative energies of the species with the central element-to-nitrogen ratio of 1:5 are much lower than those of the species with the ratio of 1:25. It is suggested that the quantitative change of central element A has great influence on calculated relative energies of the studied system. The compounds $Al(N_5)_5^{2-}$ and $Al_2(N_5)_4^{2-}$ have higher relative energies and are more stable with higher TS barrier. Therefore, the compounds $Al(N_5)_5^{2-}$ and $Al_2(N_5)_4^{2-}$ are

best suitable to be used as potential HEDMs. However, the compounds $P(N_5)_5$, $P_2(N_5)_4$ and $P_3(N_5)_3$ are not.

3.3 NBO Analysis of pentazolide compounds
$A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; n = 1–3; q = +1, 0, −1, −2, and −3)

Straka and Pyykkö [25] have observed a trend that the TS barriers are higher when the N_5 unit is closer to the fully delocalized N_5^- with all the bond lengths as similar as possible. Namely, the shorter is the N_{beta}–N_{gamma}

(those leaving to become N_2), the lower is the barrier. In this paper, we have also found the similar trend among the compounds $A_n(N_5)_{6-n}^q$. But as shown in Fig. 5, the trend is not quite uniform for some herein reported compounds. Straka and Pyykkö [25] also mentioned that the stability of analogical species increases with the negative charge on the system, which is observed similarly in the present paper. Thus, a detailed NBO analysis is performed, attempting to find out the possible explanation for this observation. Table 1 shows the number of transferred charges (N_{tc}) from the N_2 molecule after breaking the N_5 ring when compounds $A_n(N_5)_{6-n}^q$ are decomposed. The correlation between TS barriers (E_{ts}) and number of the transferred charges (N_{tc}) is plotted in Fig. 6.
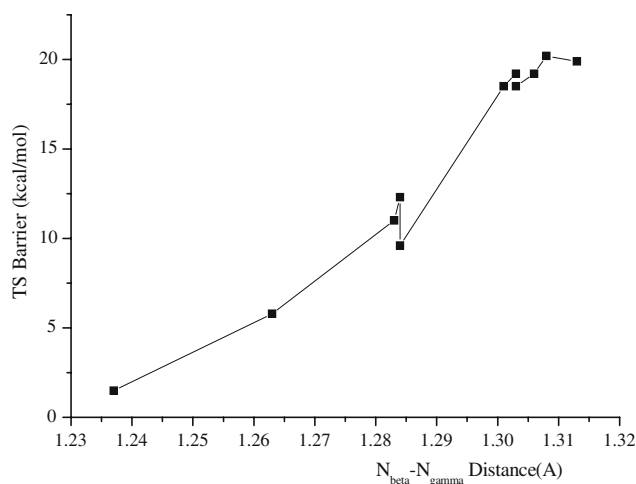
Fig. 5 Correlation between TS barriers and the ground-state $N_{beta} - N_{gamma}$ distances in the studied systems
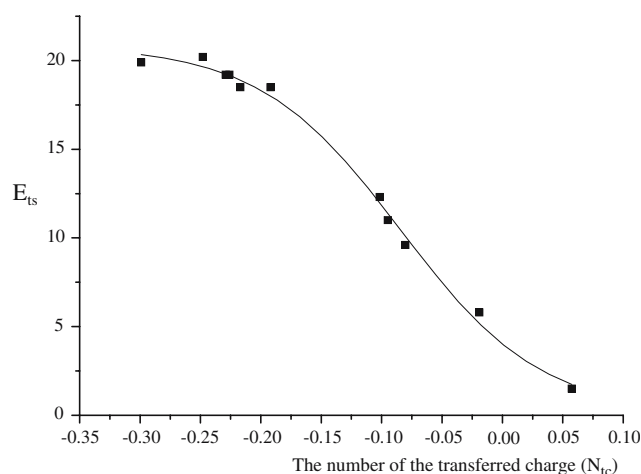
Fig. 6 Correlation between TS barriers (E_{ts}) and the number of the transferred charges (N_{tc}) from the N_2 molecule after breaking the N_5 ring in the studied systems

From Table 1 and Fig. 6, the more negative charge is transferred from the N_2 molecule after breaking the N_5 ring, the higher the TS barrier is. For example, when $Al_3(N_5)_3^{2-}$ is decomposed, the transferred charge is -0.25. Its TS barrier is 20.2 kcal/mol. However, the transferred charges is only -0.02 when neutral compound $P(N_5)_5$ is decomposed and its TS barrier is fairly low (5.8 kcal/mol). The cationic compound $S(N_5)_5^+$ has a positive transferred charge 0.06, and its TS barrier is nearly zero. Namely, the more negative charges is transferred, the higher active energy is required, and the more stable pentazolide compound is towards the decomposition. Thus, in our present paper, the negative charge transfer might play a key role when the $A_n(N_5)_{6-n}^q$ species are decomposed. It is reasonable that the more negative charge is on the system, the more negative charge is distributed on N atoms, due to the strong electronegativity of N atom. Therefore the stability of the studied systems increases with the negative charge on the system.

4 Summary

In the present paper, several pentazolide compounds $A_n(N_5)_{6-n}^q$ (A = B, Al, Si, P, and S; $n = 1$–3; $q = +1$, 0, -1, -2, and -3) have been studied theoretically as possible HEDMs. The structures, relative energies, and TS barriers were calculated. We have drawn some conclusions as follows: (1) The TS barriers increase with the decrease of relative energies in the mono- and dinuclear $A_n(N_5)_{6-n}^q$ pentazolides. (2) The calculated relative energies are decreased greatly along with increase of the central element to-nitrogen ratio. (3) The stability of the systems increases with the negative charge on the system. (4) Moreover, based on the detailed NBO analysis of $A_n(N_5)_{6-n}^q$, it is shown the more negative charges is transferred from the N_2 molecule after breaking the N_5 ring when the $A_n(N_5)_{6-n}^q$ species are decomposed, the more stable the systems are. It indicates that the charge transfer plays an important role when the $A_n(N_5)_{6-n}^q$ species are decomposed. In conclusion, since the compounds $Al(N_5)_5^{2-}$ and $Al_2(N_5)_4^{2-}$ have higher relative energies and are more stable with higher TS barrier, they are predicted to be best suitable as potential HEDMs. However the compounds $P(N_5)_5$, $P_2(N_5)_4$ and $P_3(N_5)_3$ are not.

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