Research Article

Theoretical Investigation on Structure-Property Relationship of Asymmetric Clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1\text{–}6)\)

Deng-Xue Ma,1 Yao-Yao Wei,2 Yun-Zhi Li,2 Guo-Kui Liu,2 and Qi-Ying Xia2

1School of Materials Science and Engineering, Linyi University, Linyi 276005, China
2School of Chemistry and Chemical Engineering, Linyi University, Linyi 276005, China

Correspondence should be addressed to Guo-Kui Liu; liuguokuihappy@163.com and Qi-Ying Xia; xiaqiying@163.com

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1.Introduction

The extensive studies on boron azides are developed as these molecules have been shown to be good precursors for boron nitride (BN) film deposition [1]. The chemistry of boron azides commenced in 1954 with the synthesis of boron triazide \(\text{B}(\text{N}_3)_3\) [2]; since then, it developed slowly. In 1963, Paetzold produced trimeric \((\text{Cl}_2\text{BN}_3)_3\) from the reaction of \(\text{LiN}_3\) and \(\text{BCl}_3\) in \(\text{CH}_2\text{Cl}_2\) solution [3]. The molecular structure of dichloroboron azide containing six-membered boron nitrogen heterocycle with diazo groups bounded to nitrogen atoms was determined by Müller in 1971 [4]. Boron dihalide azides \((\text{BX}_2\text{N}_3)_3\) \((X = \text{F}, \text{Cl}, \text{or Br})\) from the reaction of \(\text{BCl}_3\) with trimethylsilyl azide in \(\text{CH}_2\text{Cl}_2\) solution were also recorded by Wiberg et al. in 1972 [5]. Dehnicke reported the infrared spectra of the monoazide products, \(\text{I}_2\text{MN}_3\) \((\text{M} = \text{B}, \text{Al}, \text{Ga})\), and observed the formation of oligomers of these species in 1978 [6]. Several alkyl and arylboron azides have been synthesized using similar methods. Oligomerization for \(\text{Me}_2\text{BN}_3\) was established by \(^{11}\text{B}\) NMR spectroscopy in 1966 [7]. The chemistry of alkylboron azides was further investigated, and the development of this field has been reviewed by Paetzold, Fraenk, and coworkers [8–16]. Although the chemistry of boron azides in the condensed phase has been extensively discussed in the literature, research studies of these species in the gas phase are rather limited. With the goal to use boron azides as the single-source precursors (SSP), knowledge of their gas phase stability and thermodynamic properties becomes essential. The structure of monomers \(\text{Cl}_2\text{BN}_3\) and \((\text{CH}_3)_2\text{BN}_3\) has been explored using ab initio calculation, and the thermodynamic stabilities of \(\text{X}_2\text{BN}_3\) with respect to its dimerization and trimerization have been gained and discussed [17–20] from the theoretical view. Previous theoretical studies of the boron azides mostly focused on the symmetric boron azides.

The effect for the break of the symmetry of substituted boron azides is hardly considered. Here, in accordance with previous theoretical studies on the asymmetric clusters of inorganic boron azides [21, 22], and experimental studies on the asymmetric clusters of organic gallane azides and aluminum azides \((\text{RR'}\text{MN}_3)_n\) \((\text{M} = \text{Al}, \text{Ga}; \text{R} = \text{CH}_3; \text{R}' = \text{H, Cl, Br}; n = 3\text{–}4)\) [23, 24], the structure, stability, IR spectra, and...
thermodynamic characteristics of the asymmetric clusters of organic boron azides \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1–6)\) were theoretically discussed in detail. These discussions will provide fundamental data and references for experimentalist to design and synthesize the novel boron azides in the future.

2. Computational Methods

As is well known, it is important to choose an appropriate basis set to give the accurate description of clusters’ structures and energies. Usually, a substantial size of basis set is required. However, the size of clusters studied in this work excluded the use of a very large basis set, and hence, all calculations were performed using the DFT-B3LYP method with the 6-31G* basis set [25, 26] via the Gaussian 09 program package with the default convergence thresholds [27]. To ensure the adequacy of this basis set, we also optimized the clusters with the 6-311+G* basis set. As shown later on, results obtained from these two basis sets were similar except for slightly numerical differences. The energies of all clusters were also evaluated using the 6-311+G* basis set previously determined, such as \((\text{F}_2\text{BN}_3)_3\) (1.616 Å) [19] and \((\text{C}_6\text{F}_5\text{B(N}_3)_2)_3\) (1.60 Å) [12]. The B–C and B–F bond lengths are in the range of 1.585–1.596 Å and 1.363–1.381 Å, respectively. The computed structural parameters of the azide units in the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\) are 1.240–1.255 Å for \(\text{N}_\alpha–\text{N}_\beta\) bond lengths, 1.128–1.133 Å for \(\text{N}_\beta–\text{N}_\gamma\) bonds, and 177.1–179.4° for \(\text{N}_\alpha–\text{N}_\beta–\text{N}_\gamma\) bond angle. It is obvious that the azide group is nearly linear. Through the above discussions, it is obvious that \(\text{N}_\alpha–\text{N}_\beta\) bond is shorter than \(\text{N}_\alpha–\text{N}_\gamma\) bond length at 1.240 Å. The \(\text{N}_\beta–\text{N}_\gamma\) bond length is between N–N double (1.25 Å) and N–N triple bonds (1.10 Å). For \(n = 2–6\), the computed B–N bond length of 1.601–1.638 Å possesses typical character of B–N single bond, which is similar to the B–N length of other covalent boron azides.

3. Results and Discussion

3.1. Structures and Charge Distribution. A number of isomers are calculated at each size. Here, structures of clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1–6)\) having the lowest energy were focused because all properties of clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1–6)\) were calculated based on the lowest energy. Two stable structures of the monomer \(\text{CH}_3\text{FBN}_3\) were obtained (connectivity: \(\text{CH}_3\text{FB}–\text{N}_\alpha–\text{N}_\beta–\text{N}_\gamma\)) with a slight difference in geometrical parameters. The clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\) are produced by the head-to-tail oligomerization of the \(\text{CH}_3\text{FBN}_3\) monomers, which is a starting point for the oligomerizations. Two dimers, seventeen trimers, sixty-four tetramers, two hundred and fifty-six pentamers, and five hundred and thirty-six hexamers are obtained in this manner. Judged by the total energies, the most stable isomers at each size are labeled as 1, 2, 3, 4, 5, and 6 and shown in Figure 1. Obviously, B and \(\text{N}_\alpha\) atoms easily bond together, and B–B and \(\text{N}_\alpha–\text{N}_\beta\) bonds are not formed in the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\). In other words, the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\) contain cyclic \((\text{BN}_3)_2\)\(_n\) structures with alternating boron and \(\alpha\)-nitrogen atoms.

The corresponding geometrical parameters are collected in Table 1, and the data in parentheses are calculated results from the 6-311+G* basis set. The results obtained from different basis sets are generally consistent. In detail, bond lengths (except for B–F bonds) from the 6-311+G* basis set are slightly shorter than those from the 6-31G* basis set. This whole agreement shows that it is appropriate to choose the 6-31G* basis set to compute the titled systems. Therefore, in this work, we only report the geometrical parameters obtained with the 6-31G* basis set. For \(n = 1\), the azide group in the monomer \(\text{CH}_3\text{FBN}_3\) is slightly bent with a \(\text{N}_\alpha–\text{N}_\beta–\text{N}_\gamma\) angle of 173.1°. The calculated B–N bond length of 1.447 Å is between B–N single (1.58 Å) and double bonds (1.37 Å). The \(\text{N}_\beta–\text{N}_\gamma\) bond length at 1.135 Å is shorter than the \(\text{N}_\alpha–\text{N}_\beta\) bond length at 1.240 Å. The \(\text{N}_\beta–\text{N}_\gamma\) bond length is between N–N double (1.25 Å) and N–N triple bonds (1.10 Å). For \(n = 2–6\), the computed B–N bond length of 1.601–1.638 Å possesses typical character of B–N single bond, which is similar to the B–N length of other covalent boron azides. The computed structural parameters of the azide units in the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\) are 1.240–1.255 Å for \(\text{N}_\alpha–\text{N}_\beta\) bond lengths, 1.128–1.133 Å for \(\text{N}_\beta–\text{N}_\gamma\) bonds, and 177.1–179.4° for \(\text{N}_\alpha–\text{N}_\beta–\text{N}_\gamma\) bond angle. Therefore, the calculation method in this work is reliable, and it gives credence to our computed structural parameters of clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2–6)\).

Through the above discussions, it is obvious that \(\text{N}_\beta–\text{N}_\gamma\) bond is shorter than \(\text{N}_\alpha–\text{N}_\beta\) bond in the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1–6)\). This can be interpreted as a higher bond order for the terminal N–N bond, showing a pre-formation of the \(\text{N}_2\) molecule. Moreover, the cluster size \(n\) has an important effect on the geometries. An obvious increase is shown for the length of B–N\(_\alpha\) bond with cluster size \(n\) increasing from 1 to 2–6 owing to the tension of the ring. However, B–N\(_\beta\) bond length shows little change with cluster size in the range of 2–6, which fluctuates in the range of 1.601–1.638 Å. The \(\text{N}_\alpha–\text{N}_\beta\) bond lengths increase as the cluster size \(n\) increases from 1 to 5 and show little change from \(n = 5\) to \(n = 6\). Similarly, when cluster size \(n\) increases from 1 to 3, the B–C and B–F bond lengths increase. However, the change of B–C and B–F bond lengths is not obvious from \(n = 4\) to \(n = 6\). The \(\text{N}_\beta–\text{N}_\gamma\) bond length shortens from 1.135 Å in cluster size with 1 to 1.129 Å in cluster size with 6 and tends to be constant around 1.130 Å with \(n = 3–6\). Compared with monomer 1, the increasing bond lengths of \(\text{N}_\alpha–\text{N}_\beta\), B–C and B–F bonds that are outside of rings show that \(\text{N}_2\) \((\text{N}_\beta–\text{N}_\gamma)\), \text{CH}_3, and F groups can be easily removed to yield BN material.

To give a deeper understanding on these structures, we calculate the charge distribution of the clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1–6)\) as shown in Table 2. It can be seen that the charge distribution of \(\text{CH}_3\text{FBN}_3\) molecule exhibits zwitterionic
characteristics with the charge centers of N and B atoms, respectively. As for \((\text{CH}_3\text{FBN}_3)_n\) \((n = 2 - 6)\), charge distributions are similar to those of \(\text{CH}_3\text{FBN}_3\). However, because B atoms in these molecules all reach the high coordination, the characteristic of zwitterionic ion for these clusters is a problem needing more studies.

3.2. Relative Stabilities. All energies are displayed in Table 3, and the data in parentheses are from the 6-311 + G* basis set. Obviously, the energies obtained at the B3LYP/6-31G* levels are similar to those obtained with the 6-311 + G* basis set. The use of larger basis sets has no significant influence on the binding energies, which again shows that the 6-31G* basis

**Figure 1:** Structures of the asymmetric clusters \((\text{CH}_3\text{FBN}_3)_n\) \((n = 1-6)\).
we only report the relative stability of the clusters (CH$_3$FBN$_3$) with the 6-31G set is suitable for the clusters studied here. ©j_hus, in this work, a©j_he data in parentheses are from 6-311+G ($\alpha$) optimized at the DFT-B3LYP level.

Table 1: Ranges of the bond lengths (Å) and bond angles (deg) for the most stable structures of the asymmetric clusters (CH$_3$FBN$_3$) ($n$) ($n = 1$–6) optimized at the DFT-B3LYP level$^a$.

|   | 1     | 2     | 3     | 4     | 5     | 6     |
|---|-------|-------|-------|-------|-------|-------|
| $N_a$-N$_p$ | 1.135 | 1.133 | 1.128–1.133 | 1.133 | 1.128–1.133 | 1.129 |
| ($1.126$) | ($1.125$) | ($1.120$–1.125) | ($1.121$) | ($1.119$–1.124) | ($1.120$) |
| $N_a$-N$_\beta$ | 1.240 | 1.240 | 1.243–1.246 | 1.248 | 1.246–1.255 | 1.251 |
| ($1.236$) | ($1.235$) | ($1.240$–1.249) | ($1.246$) | ($1.243$–1.253) | ($1.250$) |
| $N_a$-B | 1.447 | 1.633 | 1.614–1.638 | 1.601–1.602 | 1.608–1.637 | 1.606 |
| ($1.442$) | ($1.641$–1.643) | ($1.613$–1.632) | ($1.598$–1.600) | ($1.603$–1.627) | ($1.601$–1.604) |
| B–C | 1.563 | 1.585 | 1.589–1.593 | 1.591 | 1.591–1.596 | 1.592 |
| ($1.555$) | ($1.579$) | ($1.584$–1.588) | ($1.587$) | ($1.587$–1.591) | ($1.588$) |
| B–F | 1.341 | 1.363 | 1.376–1.381 | 1.385 | 1.380–1.386 | 1.387–1.388 |
| ($1.349$) | ($1.374$) | ($1.388$–1.393) | ($1.397$) | ($1.387$–1.398) | ($1.398$–1.399) |
| C–H | 1.093–1.098 | 1.096–1.098 | 1.094–1.098 | 1.094–1.098 | 1.093–1.098 | 1.094–1.098 |
| ($1.091$–1.096) | ($1.094$–1.096) | ($1.094$–1.096) | ($1.094$–1.096) | ($1.091$–1.096) | ($1.093$–1.096) |
| $N_a$-B–N$_a$ | 94.1 | 124.7–125.2 | 126.7–126.9 | 126.3–128.2 | 125.2–125.3 |
| ($95.2$) | ($123.9$–125.0) | ($127.1$) | ($125.6$–131.2) | ($126.0$–126.1) |
| $N_a$-N$_p$–B | 85.9 | 100.2–100.7 | 102.9–103.1 | 105.0–107.8 | 106.2–106.6 |
| ($84.8$) | ($99.3$–100.7) | ($103.3$) | ($104.1$–106.4) | ($106.6$–106.7) |
| $N_a$-N$_p$–N$_p$ | 121.3 | 123.3–124.6 | 117.6–119.6 | 114.9–118.4 | 115.5–118.7 |
| ($121.4$) | ($125.6$–125.8) | ($115.6$–119.4) | ($118.0$–118.6) | ($113.3$–118.0) |
| $N_a$-N$_p$–N$_\beta$ | 173.1 | 177.1 | 177.8–178.9 | 178.3–178.4 | 178.2–179.4 |
| ($173.3$) | ($177.5$) | ($178.1$–179.1) | ($178.3$–178.4) | ($178.3$–179.4) |

$^a$The data in parentheses are from 6-311+G$^*$ basis set.

Table 2: Atomic charge (e) of the most stable structure (CH$_3$FBN$_3$)$_n$ ($n = 1$–6).

|   | 1     | 2     | 3     | 4     | 5     | 6     |
|---|-------|-------|-------|-------|-------|-------|
| $N_a$ | −0.5840 | −0.5922 | −0.5847 | −0.5885 | −0.5854 | −0.5918 |
| $N_p$ | 0.2447 | 0.2761 | 0.2760 | 0.2753 | 0.2704 | 0.2686 |
| $N_\beta$ | −0.0175 | 0.0299 | 0.0512 | 0.0602 | 0.0608 | 0.0673 |
| B | 1.1319 | 1.0869 | 1.0721 | 1.0745 | 1.0773 | 1.0809 |
| F | −0.4760 | −0.4973 | −0.5100 | −0.5174 | −0.5171 | −0.5227 |
| C | −1.0830 | −1.0571 | −1.0545 | −1.0551 | −1.0568 | −1.0561 |
| H | 0.2627 | 0.2512 | 0.2499 | 0.2504 | 0.2503 | 0.2503 |

Table 3: Total energies (E), zero point energy (ZPE), uncorrected binding energies ($E_b$), corrected binding energies ($E_{b-c}$), average corrected binding energy ($E_{b-c,ave}$), and second-order energy difference ($\Delta_2E$) (unit: kJ·mol$^{-1}$)$^a$.

| Clusters | E  | $E_b$  | ZPE  | $E_{b-c}$  | $E_{b-c,ave}$  | $\Delta_2E$  |
|----------|----|--------|------|------------|----------------|--------------|
| 1        | −865344.11 | 150.49 | (−863796.61) | 149.36 |
| 2        | −1727098.45 | 10.23 | 306.95 | (−1727602.68) | (9.45) | (304.09) | (4.30) | (2.15) | (199.36) |
| 3        | −2590684.89 | 52.56 | 466.36 | (−2591439.62) | (49.78) | (462.16) | (36.26) | (12.09) | (16.97) |
| 4        | −3454250.88 | 74.44 | 624.01 | (−3455257.97) | (71.51) | (618.54) | (53.27) | (12.81) | (5.01) |
| 5        | −4317819.67 | 99.12 | 780.67 | (−4319078.66) | (95.59) | (772.93) | (72.03) | (14.10) | (5.01) |
| 6        | −5181384.41 | 119.75 | 937.24 | (−5182894.97) | (115.28) | (927.98) | (86.82) | (14.47) | (5.01) |

$^a$The data in parentheses are from 6-311+G$^*$ basis set.
The calculated energy is also plotted as a function of cluster size. The zero point energies of the most stable clusters (CH3FBN3) and ZPE (CH3FBN3) represent the zero point energies of the most stable clusters (CH3FBN3) and ZPE (CH3FBN3) respectively, and the 0.96 is a scaling factor [28].

From Table 3, the ratios of ZPE corrections to their binding energies are large for the clusters (CH3FBN3)n (n = 2–6). Thus, it is necessary to carry out the ZPE corrections for the binding energies. For intuitive presentation, Figure 2(d) is seen to increase monotonically with the augment of cluster size n, which means that clusters can continue to gain energy during the clusters’ growth process. The E_b-c values increase sharply with the clusters size n from 2 to 3; then, it approaches to be stable around 3.4.1 Thermodynamic Properties. Thermodynamic functions are important parameters for clusters to predict reactive
property in a chemical reaction. According to vibrational analysis and statistical thermodynamic method, the standard molar heat capacity \( (C_p,m) \), standard molar thermal entropy \( (S_m) \), and standard molar thermal enthalpy \( (H_m) \) of the asymmetric clusters \((\text{CH}_3\text{FBN}_3)_n \) \((n = 1 \text{ – 6})\) in the range of 200–800 K are evaluated and tabulated in Table 4. It is obvious that the calculated thermodynamic functions increase with the temperature \( T \) raising. For more clear intuitive, taking monomer 1 as an example, the temperature-dependent relationships for \( C_p,m, S_m, \) and \( H_m \) are expressed in formulas (2)–(4) and all are plotted in Figure 4(a). These correlations approximate to linear equations due to the small coefficients of \( T^2 \); namely, the \( C_p,m, S_m, \) and \( H_m \) increase linearly with the increase of temperature \( T \). This can be understood from the fact that these three thermodynamic functions are dominated by the weak translational and rotational motions of the clusters at lower temperature, whereas the vibrational motion is intensified and makes more contributions to \( C_p,m, S_m, \) and \( H_m \) at higher temperature. The same linear relationships are found for clusters \((\text{CH}_3\text{FBN}_3)_n \) with \( n = 2 \text{ – 6} \):

\[
C_p,m = 33.4650 + 0.2460 \, T - 1.1698 \times 10^{-4} \, T^2, \\
R^2 = 0.9999, \\
\text{SD} = 0.3318,
\]

\[
S_m = 231.0291 + 0.4049 \, T - 1.4317 \times 10^{-4} \, T^2, \\
R^2 = 0.9998, \\
\text{SD} = 0.9034,
\]

\[
H_m = -3.6904 + 0.0606 \, T + 6.401 \times 10^{-5} \, T^2, \\
R^2 = 0.9999, \\
\text{SD} = 0.2784,
\]  

where \( R^2 \) represents the square of correlation coefficient and SD represents standard deviation.

Moreover, the cluster size-dependent relationships for \( C_p,m, S_m, \) and \( H_m \) are expressed in formulas (5)–(7) and all are shown in Figure 4(b). All thermodynamic functions increase monotonically with the enlarged cluster size \( n \); in other words, when one more \( \text{CH}_3\text{FBN}_3 \) is bound, the \( C_p,m, S_m, \) and \( H_m \) increase with the average of 108 J·mol\(^{-1}\)·K\(^{-1}\), 133 J·mol\(^{-1}\)·K\(^{-1}\), and 18 kJ·mol\(^{-1}\), separately. This means that the contribution of monomer \( \text{CH}_3\text{FBN}_3 \) to the thermodynamic properties of cluster matches the cluster additivity:

\[
C_p,m = -12.0847 + 108.4637 \, n, \\
R^2 = 1.0000, \\
\text{SD} = 1.0282,
\]

\[
S_m = 211.0987 + 133.2237 \, n, \\
R^2 = 0.9996, \\
\text{SD} = 8.0272,
\]

\[
H_m = 1.0620 + 18.3966 \, n, \\
R^2 = 0.9999, \\
\text{SD} = 0.5260.
\]
In addition, the theoretical enthalpies (\( \Delta H \)) and Gibbs free energies (\( \Delta G \)) of various oligomerizations from monomer \( \text{CH}_3\text{FBN}_3 \) in the range of 200–800 K are compiled in Table 5. The values of \( \Delta H \) in the processes are negative except for the process 1 \( \rightarrow \) 2 beyond 700 K, indicating that these oligomerization processes are exothermic. The \( \Delta G \) at a given temperature is evaluated by the equation \( \Delta G = \Delta H - T \Delta S \). The values of \( \Delta G \) are all positive, which

Figure 3: IR spectra of the asymmetric clusters \( (\text{CH}_3\text{FBN}_3)_n \) \( (n = 1 - 6) \) with full width at half maxima of 20 cm\(^{-1}\).
reveals the oligomerizations cannot occur spontaneously in the range of 200–800 K. There are no experimentally thermodynamic data available for the asymmetric clusters (CH$_3$FBN$_3$)$_n$ ($n$ = 1 – 6), so the calculated thermodynamic functions and the obtained relationships of them with the temperature and cluster size $n$ may help the experiment to further study the physical, chemical, and energetic properties of the asymmetric clusters (CH$_3$FBN$_3$)$_n$ ($n$ = 1 – 6) or other asymmetric boron azides.

3.5. Aromatic Properties. Here, the aromaticity of the studied systems will be discussed. Because our systems are nonplanar, it is not suitable to use the criterion of nucleus-independent chemical shift (NICS) [30]. In order to find out whether a large $\pi$ bond exists in our studied system, we use the newly proposed localized orbital locator (LOL)-$\pi$ method [31] that can be used for studying nonplanar systems to study the $\pi$ bonds of our systems. The LOL-$\pi$ is analyzed and visualized with the Multiwfn [32]. From Figure 5, there

| $n$ | $T$ (K) | $C^\theta_{p,m}$ ($\text{J mol}^{-1} \text{K}^{-1}$) | $S^\theta_m$ ($\text{J mol}^{-1} \text{K}^{-1}$) | $H^\theta_m$ (kJ mol$^{-1}$) |
|-----|---------|----------------|----------------|----------------|
| 1   | 200     | 77.73          | 305.18         | 11.30          |
|     | 298.2   | 96.48          | 339.77         | 19.87          |
|     | 400     | 113.47         | 370.57         | 30.58          |
|     | 500     | 127.30         | 397.42         | 42.65          |
|     | 600     | 138.62         | 421.66         | 55.96          |
|     | 700     | 147.95         | 443.75         | 70.30          |
|     | 800     | 155.71         | 464.03         | 85.50          |
| 2   | 200     | 161.34         | 409.57         | 19.88          |
|     | 298.2   | 206.04         | 482.65         | 38.00          |
|     | 400     | 243.12         | 548.58         | 60.94          |
|     | 500     | 271.97         | 606.05         | 86.75          |
|     | 600     | 295.00         | 657.75         | 115.14         |
|     | 700     | 313.71         | 704.68         | 145.61         |
|     | 800     | 329.19         | 747.61         | 177.78         |
| 3   | 200     | 242.25         | 509.21         | 28.47          |
|     | 298.2   | 312.13         | 733.64         | 55.81          |
|     | 400     | 369.54         | 868.53         | 90.64          |
|     | 500     | 413.90         | 986.27         | 129.90         |
|     | 600     | 449.12         | 1092.19        | 173.12         |
|     | 700     | 477.62         | 1276.18        | 219.50         |
|     | 800     | 501.12         | 1573.18        | 268.47         |
| 4   | 200     | 326.44         | 584.95         | 37.13          |
|     | 298.2   | 420.82         | 733.64         | 55.81          |
|     | 400     | 497.89         | 868.53         | 90.64          |
|     | 500     | 557.25         | 986.27         | 129.90         |
|     | 600     | 604.30         | 1092.19        | 173.12         |
|     | 700     | 642.35         | 1276.18        | 219.50         |
|     | 800     | 673.70         | 1573.18        | 268.47         |
| 5   | 200     | 411.59         | 686.62         | 46.56          |
|     | 298.2   | 530.37         | 874.08         | 93.03          |
|     | 400     | 627.05         | 1044.02        | 152.18         |
|     | 500     | 701.33         | 1192.26        | 218.74         |
|     | 600     | 760.11         | 1325.52        | 291.93         |
|     | 700     | 807.59         | 1446.38        | 370.39         |
|     | 800     | 846.71         | 1556.85        | 453.17         |
| 6   | 200     | 496.46         | 788.60         | 55.96          |
|     | 298.2   | 639.39         | 1014.65        | 111.99         |
|     | 400     | 755.59         | 1219.48        | 183.27         |
|     | 500     | 844.78         | 1398.06        | 263.47         |
|     | 600     | 915.34         | 1558.56        | 351.61         |
|     | 700     | 972.33         | 1704.09        | 446.09         |
|     | 800     | 1019.26        | 1837.08        | 545.74         |

$^a$Units: $T$ (K), $C^\theta_{p,m}$ (J mol$^{-1}$ K$^{-1}$), $S^\theta_m$ (J mol$^{-1}$ K$^{-1}$), and $H^\theta_m$ (kJ mol$^{-1}$).

Figure 4: Variations of the thermodynamic functions ($C^\theta_{p,m}$, $S^\theta_m$, and $H^\theta_m$) with the temperature ($T$) (a) for the monomer CH$_3$FBN$_3$ and the cluster size $n$ (b) and for the asymmetric clusters (CH$_3$FBN$_3$)$_n$ ($n$ = 1–6).
|       | $T$   | 200   | 298.2 | 400   | 500   | 600   | 700   | 800   |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 2(1)→(2) | $\Delta H$ | -7.22 | -6.24 | -4.72 | -3.05 | -1.28 | 0.51  | 2.28  |
|       | $\Delta G$ | 32.94 | 52.45 | 72.30 | 91.35 | 110.06| 128.48| 146.64|
| 3(1)→(3) | $\Delta H$ | -43.70| -42.07| -39.37| -36.32| -33.03| -29.67| -26.30|
|       | $\Delta G$ | 37.57 | 77.11 | 117.48| 156.31| 194.54| 232.21| 269.37|
| 4(1)→(4) | $\Delta H$ | -61.34| -58.75| -54.65| -50.05| -45.13| -40.09| -35.04|
|       | $\Delta G$ | 65.81 | 127.69| 190.85| 251.66| 311.54| 370.60| 428.91|
| 5(1)→(5) | $\Delta H$ | -81.97| -78.35| -72.75| -66.54| -59.90| -53.14| -46.36|
|       | $\Delta G$ | 85.89 | 167.51| 250.78| 330.88| 409.77| 487.52| 564.28|
| 6(1)→(6) | $\Delta H$ | -98.66| -94.05| -87.03| -79.25| -70.97| -62.53| -54.08|
|       | $\Delta G$ | 109.84| 211.20| 314.55| 413.98| 511.87| 608.36| 703.60|

*Units: $T$ (K), $\Delta H$ (kJ·mol$^{-1}$), and $\Delta G$ (kJ·mol$^{-1}$).

**Figure 5**: LOL-$\pi$ isosurface of different systems with the isovalue of 0.4.
is $\pi$ bond of NNNB in 1 and similar $\pi$ bonds in 2-6. However, the $\pi$ conjugation of 2-6 is not as good as that of 1. Meanwhile, Figure 5 also shows no large $\pi$ bonds in all systems.

4. Conclusions

We have systematically studied the structure, relative stability, IR, and thermodynamic properties of the asymmetric clusters (CH$_3$FBN$_3$)$_n$ ($n = 1-6$) at the DFT-B3LYP/6-31G*. The B and N$_a$ atoms tend to bond together in clusters (CH$_3$FBN$_3$)$_n$ ($n = 2-6$). The variation trend of geometrical parameters shows N$_2$ (N$_b$–N$_a$), –CH$_3$, and F groups are easily eliminated and BN material is yielded. The calculated $\Delta_E$ of the asymmetric clusters (CH$_3$FBN3) $n$ ($n = 1-6$) exhibits a pronounced odd-even alternation phenomenon with cluster size $n$ increasing, indicating that the cluster at $n = 3$ is more stable than other clusters. From monomer ($n = 1$) to clusters ($n = 2-6$), the N$_3$ asymmetric stretching vibration presents blue-shifted trend while the N$_3$ symmetric stretching vibration and –CH$_3$ stretching vibration are red-shifted.

©j_he thermo-demonstrate that the formation of clusters (CH$_3$FBN$_3$)$_n$ trend while the N$_3$ symmetric stretching vibration and asymmetric clusters (CH$_3$FBN$_3$)$_n$ presents blue-shifted. ©j_he Band N

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References

[1] R. L. Mulinax, G. S. Okin, and R. D. Coombe, “Gas phase synthesis, structure, and dissociation of boron triazole,” The Journal of Physical Chemistry, vol. 99, no. 17, pp. 6294–6300, 1995.
[2] E. Wiberg and H. Michaud, “Notizen: zur kenntnis eines methylaluminiumdiazids CH$_3$Al(N$_3$)$_2$,” Zeitschrift für Naturforschung B, vol. 9, no. 7, p. 497, 1954.
[3] P. I. Paetzold, “Beiträge zur chemie der bor-azide. i. zur kenntnis von dichlorborazid,” Zeitschrift für Anorganische und Allgemeine Chemie, vol. 326, no. 1-2, pp. 47–52, 1963.
[4] U. Müller, “Die kristall-und molekularstruktur von bordichlorazid (BCl$_3$N$_3$)$_3$,” Zeitschrift für Anorganische und Allgemeine Chemie, vol. 382, no. 2, pp. 110–122, 1971.
[5] N. Wiberg, W.-Ch. Joo, and K. H. Schmid, “Über einige azide des berylliums, magnesiums, bors und aluminiums (zur reaktion von silylaziden mit elementhalogeniden),” Zeitschrift für Anorganische und Allgemeine Chemie, vol. 394, no. 1-2, pp. 197–208, 1972.
[6] K. Dehnicke and N. Krüger, “Dijodo- und dibromometallazide X$_2$MN$_3$ von aluminium und gallium,” Zeitschrift für organische und allgemeine Chemie, vol. 444, no. 1, pp. 71–76, 1978.
[7] P. I. Paetzold and H.-J. Hansen, “Beiträge zur chemie der bor-azide. VI. zur kenntnis von dimethylborazid und seinen aminaten,” Zeitschrift für Anorganische und Allgemeine Chemie, vol. 345, no. 1-2, pp. 79–86, 1966.
[8] J. Müller, P. Paetzold, and R. Boese, “The reaction of deca-boron with hydrazic acid: a novel access to azaboranes,” Heteroatom Chemistry, vol. 1, no. 6, pp. 461–465, 1990.
[9] P. I. Paetzold, P. P. Haberereder, and R. Müllbauer, “Beiträge zur chemie der borazide VII. darstellung und eigenschaften von diorganylboraziden,” Journal of Organometallic Chemistry, vol. 7, no. 1, pp. 45–50, 1967.
[10] P. I. Paetzold, P. P. Haberereder, and R. Müllbauer, “Beiträge zur chemie der borazide VIII. Thermisscher zerfall von diorganylboraziden,” Journal of Organometallic Chemistry, vol. 7, no. 1, pp. 51–60, 1967.
[11] W. Fraenk, T. M. Klapotke, B. Krumm, and P. Mayer, “Bis(pentafluorophenyl)boron azide: synthesis and structural characterization of the first dimeric boron azide,” Chemical Communications, vol. 8, no. 8, pp. 667–668, 2000.
[12] W. Fraenk, T. M. Klapotke, B. Krumm, H. Nöth, M. Suter, and M. Warchhold, “Oligomeric pentafluorophenylboron azides,” Journal of the Chemical Society, Dalton Transactions, no. 24, pp. 4635–4638, 2000.
[13] W. Fraenk, T. Haberereder, A. Hammer el al., “Highly energetic tetraazidoborate anion and boron triazole adducts,” Inorganic Chemistry, vol. 40, no. 6, pp. 1334–1340, 2001.
[14] P. I. Paetzold, “Darstellung, eigenschaften und zerfall von boraziden,” in Anorganische Chemie. Fortschriften der Chemischen Forschung, vol. 8/3, pp. 437–469, Springer, Berlin, Germany, 2006.
[15] P. I. Paetzold, M. Gayoso, and K. Dehnicke, “Darstellung, Eigenschaften und Schwingungsspektern der trimeren Bor-dihalogenidazide (BCl$_3$N$_3$)$_3$ und (BBr$_3$N$_3$)$_3$,” Chemische Berichte, vol. 98, no. 4, pp. 1173–1180, 1965.
[16] M. J. Travers and J. V. Gilbert, “UV absorption spectra of intermediates generated via photolysis of B(N$_3$)$_3$, BCl(N$_3$)$_3$, and BCl$_3$(N$_3$)$_3$ in low-temperature argon matrices,” The Journal of Physical Chemistry A, vol. 104, no. 16, pp. 3780–3785, 2000.
[17] R. Hausser-Wallis, H. Oberhammer, W. Einholz, and P. O. Paetzold, "Gas-phase structures of dimethylboron azide and dimethylboron isocyanate. Electron diffraction and ab initio study," *Inorganic Chemistry*, vol. 29, no. 17, pp. 3286–3289, 1990.

[18] L. A. Johnson, S. A. Sturgis, I. A. Al-Jihad, B. Liu, and J. V. Gilbert, "Low-temperature matrix isolation and photolysis of BCl\textsubscript{3}N\textsubscript{3}:\spectroscopic identification of the photolysis product CIBNCl," *The Journal of Physical Chemistry A*, vol. 103, no. 6, pp. 686–690, 1999.

[19] W. Fraenck and T. M. Klapötke, "Theoretical studies on the thermodynamic stability and trimerization of BF\textsubscript{2}N\textsubscript{3}," *Journal of Fluorine Chemistry*, vol. 111, no. 1, pp. 45–47, 2001.

[20] D. X. Ma, Q. Y. Xia, and C. Zhang, "Theoretical studies on structural feature and thermodynamic stability of F\textsubscript{3}BN\textsubscript{3} oligomers," *Journal of Atomic and Molecular Physics*, vol. 26, no. 2, pp. 361–367, 2009.

[21] A. Wang, Z. Chen, D. Ma, and Q. Xia, “The search for the structures, stabilities, IR spectra, and thermodynamic properties of the asymmetric clusters (HCIBN\textsubscript{n}) n (n = 1 – 6)," *Russian Journal of Physical Chemistry A*, vol. 90, no. 13, pp. 2541–2549, 2016.

[22] Q. Y. Xia, D. X. Ma, D. J. Li, B. H. Li, X. Q. Wang, and G. F. Ji, "The molecular designs and properties of asymmetric heterocycles (HBrBN\textsubscript{n}) n (n = 1 – 4)," *Journal of Structural Chemistry*, vol. 56, no. 8, pp. 1468–1473, 2015.

[23] J. Kouvetakis, J. McMurray, C. Steffek, T. L. Groy, and J. L. Hubbard, "Synthesis and structures of heterocyclic azidogallanes [(CH\textsubscript{3})ClGaN\textsubscript{3}] and [(CH\textsubscript{3})BrGaN\textsubscript{3}] en route to [(CH\textsubscript{3})HGaN\textsubscript{3}]: an inorganic precursor to GaN," *Inorganic Chemistry*, vol. 39, pp. 3805–3809, 2000.

[24] J. Kouvetakis, J. McMurray, C. Steffek, T. L. Groy, J. L. Hubbard, and L. Torrisson, "Synthesis of new azidogallanes with heterocyclic molecular structure," *Main Group Metal Chemistry*, vol. 24, no. 2, pp. 77–84, 2001.

[25] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648–5652, 1993.

[26] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, no. 2, pp. 785–789, 1988.

[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09, Revision A.02*, Gaussian, Inc., Pittsburgh, PA, USA, 2009.

[28] A. P. Scott and L. Radom, "Harmonic vibrational frequencies: an evaluation of Hartree–Fock, Møller–Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors," *The Journal of Physical Chemistry*, vol. 100, no. 41, pp. 16502–16513, 1996.

[29] E. Lieber, D. R. Levering, and L. Patterson, "Infrared absorption spectra of compounds of high nitrogen content," *Analytical Chemistry*, vol. 23, no. 11, pp. 1594–1604, 1951.

[30] G. V. Baryshnikov, B. F. Minaev, N. N. Karaush, and V. A. Minaeva, "Design of nanoscaled materials based on tetraoxa[8]circulene," *Physical Chemistry Chemical Physics*, vol. 16, no. 14, pp. 6555–6559, 2014.

[31] T. Lu and Q. Chen, "A simple method of identifying π orbitals for non-planar systems and a protocol of studying π electronic structure," *Theoretical Chemistry Accounts*, vol. 139, no. 2, p. 25, 2020.

[32] T. Lu and F. Chen, "Multiwfn: a multifunctional wavefunction analyzer," *Journal of Computational Chemistry*, vol. 33, no. 5, pp. 580–592, 2012.