Nitrogen versus carbon in planar pentacoordinate environments supported by Be₅Hₙ rings†

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NB₅Hₙ⁺⁻³ (n = 0–5) (0A–5A) species with a novel planar pentacoordinate nitrogen (ppN) were designed by the isoelectronic substitution of the C atom in planar pentacoordinate carbon (ppC) species CBe₅Hₙ⁻⁴ (n = 0–5) with an N atom. The highly flexible H atoms found in ppC species CBe₅H₂⁻ and CBe₅H₃⁻ were fixed upon the nitrogen substitution, as mirrored by the non-flexible H atoms in their ppN analogues NB₅H₂⁻ (2A) and NB₅H₃⁻ (3A). Moreover, the N atom was found to fit the H-surrounded Be₅ ring better than the C atom because the ppC species CBe₅H₄ and CBe₅H₅⁻ adopted non-planar structures due to size-mismatch between the C atom and the H-surrounded Be₅ ring, but their ppN analogues NB₅H₄⁺ (4A) and NB₅H₅²⁻ (5A) adopted perfect planar structures. The electronic structure analyses revealed that the N atoms in 0A–5A were involved in four doubly occupied orbitals, including three six-center two-electron (6c-2e) σ bonds and one 6c-2e π bond. Therefore, these ppN species not only obey the octet rule, but also possess the interesting σ and π double aromaticity, which contributes to the stabilization. Consequently, 2A, 4A, and 5A are charged kinetically viable global energy minima, and are suitable for the gas phase generation and spectroscopic characterization.

Introduction

In general, a typical main group nonmetal can have the maximum number of four closely connected atoms and they often adopt a tetrahedral arrangement as suggested by the van’t Hoff/Le Bel rule. Therefore, planar pentacoordination is especially interesting in that it violates both the highest number and the suggested arrangement of closely connected atoms. Such a non-classical bonding has mainly been observed, heretofore, in the planar pentacoordinate carbon⁴ (ppC) species. Note that though ppC stemmed from the planar tetra-⁴ and hexacoordinate carbon⁷ (pC and p6C), it played a more important role in planar carbon chemistry recently because a dozen ppC species were found to be the global energy minima (GEM), suitable for experimental realization. To our knowledge, the ppC GEMs represent more than half of known GEM planar carbon species. Their GEM nature may be the result of geometric and electronic good fitting between C atom and five-membered rings. However, exceptions can be found in the CBe₅Hₙ⁻⁴ (n = 2–5) system (see Fig. S1 in ESI†), where CBe₅H₄ and CBe₅H₅⁻ species are non-planar, suggesting that carbon is too big to stay at the center of Be₅H₄ and Be₅H₅⁻ rings preferentially.

As the heavier neighbor of carbon, nitrogen has rich chemistry, too. In particular, many non-classical bonding patterns of carbon had been extended to nitrogen.⁴ For instance, the planar tetracoordinate nitrogen (ptN) had been observed in NSiAl₃, NAl₄/NAl₄⁺, NM₄H₄⁺ (M = Cu, Ni), NAl₄⁺ (X = N, P, As), etc.⁷ Noticeably, the higher electronegativity of nitrogen than that of carbon leads to the higher preference for the localized bonding, which is unfavorable to the design of planar hypercoordinate nitrogen species. Nevertheless, Ding et al. proposed and demonstrated that this bonding preference could be utilized to design the ptC and ptN species.⁴⁸

Nonetheless, the planar pentacoordinate nitrogen (ppN) was less familiar to chemists. To the best of our knowledge, two ppN species (NCu₅H₅⁺ and NBe₅Au₅²⁻)⁶⁻⁸ had been reported, but none of them were convincingly demonstrated to be the GEM, which lowers their possibility to be observed in the experiments. Can a ppN species be a GEM and what is the difference between ppN and ppC species possessing the similar geometrical skeletons? Through design and characterization of the ppN species NB₅C₄⁻ (n = 0–5) by substituting the C atom in CBe₅Hₙ⁻⁴ (n = 0–5)⁷ with N atom, we reported in the present work the first examples of the GEM ppN species. Simultaneously, we found that nitrogen fits more nicely with the Be₅Hₙ rings than carbon and...
the nitrogen substitution for the carbon atom in ppC species CBe$_3$H$_4$ and CBe$_3$H$_5$ can fix the highly flexible H atoms.

**Computational methods**

For ppN species NBe$_5$H$_n$ (n = 0–5) (0A–5A), the geometry optimization and harmonic vibrational frequency analysis were performed at the B3LYP/aug-cc-pVTZ level. The B3LYP functional was calibrated using ab initio calculations at the MP2/aug-cc-pVTZ level, which gave the optimized structures of 1A–5A not different in essential from those optimized using B3LYP functional, suggesting that it is safe to use B3LYP to study the current system. To better understand the electronic structures, the natural bond orbital (NBO) and the adaptive natural density partitioning (AdNDP) analyses were carried out at the B3LYP/aug-cc-pVTZ level. The simulations were performed adiabatically, the initial velocity was not fixed but related to the temperatures considered, and the Hessian was recalculated every 5 gradient points.

The structural evolution during the simulations was evaluated by the root-mean-square deviation (RMSD) relative to the B3LYP/6-31G(d)-optimized geometries. The vertical detachment energy (VDE) and the vertical electron affinity (VEA) were calculated using the outer valence Green’s function (OVGF) at the OVGF/aug-cc-pVTZ level. The stochastic search algorithm was performed using GXYZ 2.0 program, the AdNDP was analyzed using AdNDP program, and the CCSD(T) calculations were carried out using MolPro 2012.1, and all other calculations were performed using the Gaussian 09 package.

**Results and discussion**

**Design of NBe$_5$H$_n$ (n = 0–5)**

The ppN species NBe$_5$H$_n$ (n = 0–5) (0A–5A, see Fig. 1) could be designed simply by isoelectronic substitution of C atom in ppC species CBe$_5$H$_n$ (n = 0–5) with N$^+$ cation. Note that 2A and 3A both have an isomer, i.e., 2A'$\text{ and } 3A'$ shown in Fig. 1, whose structural difference lies in the distribution of H atoms. According to our calculations at the CCSD(T)/B3LYP level, 2A' and 3A' are 10.9 and 9.5 kcal mol$^{-1}$ higher in energy than 2A and 3A, respectively, thus they are discarded in the following. As shown in Fig. 1, the energy minima 0A–5A adopt the perfect planar structures at the B3LYP/aug-cc-pVTZ level. In particular, the planar ppN species 4A and 5A are in sharp contrast to their quasi-planar analogues CBe$_3$H$_4$ and CBe$_3$H$_5^+$, suggesting the better match of N atom than C atom with the Be$_5$H$_4$ and Be$_5$H$_5$.
rings. The N–Be interatomic distances range from 1.557 to 1.781 Å in 0A–5A, which is short enough for each Be atom to be considered as a coordination to N atom, so 0A–5A are eligible ppN species.

Electronic structure analyses

The chemical bonding in ppN species 0A–5A are similar to their analogue ppC species CBe5Hn⁻⁴ (n = 0–5). Fig. 2 shows the AdNDP view of chemical bonding in 0A–5A. As shown in Fig. 2, for Be–Be edge without bridging H atom, there is a 2c-2e Be–Be σ bond with occupation numbers (ONs) ranging from 1.96 to 1.98 [e] (see the first column). Exposing such diffused metal-metal σ bonds may be negative to the stabilization of ppN species. In contrast, for Be–Be edge with a bridging H atom, there is a Be–H–Be three-center two-electron (3c-2e) σ bond (ON = 1.91–1.99 [e], see the second column). Though such bonds involve three centers, they are less diffused than the Be–Be 2c-2e bonds, which may be positive to the stabilization from the electronic structure point of view.

As shown in Fig. 3, the advantage to possess the Be–H–Be 3c-2e bonds can be demonstrated by the increasing HOMO–LUMO gaps from 0.44 eV for NBe₅ without bridging H to 7.93 eV with all Be–Be edges bridged by the H atoms. Note that the most obvious variation occurs at n = 4 to n = 5, which corresponds to the complete elimination of diffused Be–Be 2c-2e bond, verifying the beneficial effect of Be–H–Be 3c-2e bonds to the stabilization of the ppN structures. We also note that the HOMO–LUMO gaps of ppN species NBe₅Hₙ⁻³ (n = 0–5) are all higher than their analogue ppC species CBe₅Hₙ⁻⁴ (n = 0–5), which indicates the electronically better match of N atom than that of C atom with Be₅Hₙ rings.

Bonding patterns shown in the third column of Fig. 2 depict the interesting delocalized six-center two-electron (6c-2e) σ bonds, while those in the last column illustrate the delocalized 6c-2e π bonds. These four 6c-2e bonds are very similar in all NBe₅Hₙ⁻³ species despite of n values and they are also similar to those of their ppC analogues CBe₅Hₙ⁻⁴ (n = 0–5). The existence of these four bonds builds the basis for the stabilization of ppN arrangement from the electronic structure point-of-view. First, these four bonds fill eight electrons to the valence shell of central nitrogen atoms, i.e. the ppN species obey the octet rule. Second, three delocalized σ bonds and one delocalized π bond meet the Hückel's 4n+2 rule for n = 1 and 0, respectively, suggesting the novel 6σ + 2π double aromaticity.

The aromaticity within NBe₅ moieties of 2A–5A was evaluated using ELF analysis. As shown in Fig. S2,¹ the bifurcation values for σ bonding (ELFσ) range from 0.936 to 0.944, while that for π bonding (ELFπ) are all 0.999, thus giving the average bifurcation values (ELFavr) from 0.968 to 0.972. Since the ELFσ, ELFπ and ELFavr values are all much larger than 0.7, the threshold value for ELF criterion of aromaticity judgement,¹,²,³ the ppN species 2A–5A should be the σ, π and overall aromatic molecules.

Taking 5A as an example, we studied aromaticity by performing the NICS analysis. As shown in Fig. 4, the NICS values for almost all the examined points near the molecule are obviously negative, suggesting aromatic nature for 5A. An exception with the positive NICS value of +3.7 ppm can be found at the point located 0.5 Å above the beryllium atom, but it does not influence the aromatic nature of 5A as a whole. Note that the points with largest negative NICS values (−52.9 and −21.4 ppm) locate 0.5 and 1.0 Å above the nitrogen atom, suggesting the π electron delocalization, while the points with the second largest negative NICS values (−18.8 and −16.1 ppm) locate in the molecular plane within Be₅ ring, indicating the σ electron delocalization.

Fig. 2 AdNDP bonding patterns of 0A–5A with occupation numbers (ONs).

Fig. 3 Variation of HOMO–LUMO gaps (gaps, in eV) with the increasing number of H atoms (n) in NBe₅Hₙ⁻³ and CBe₅Hₙ⁻⁴ (n = 0–5).
delocalization. The NICS values become close to zero when the distance between the examined point and the molecule becomes long. The NICS values verify the existence of aromaticity, consistent with the conclusion from the AdNDP and ELF analyses.

The conventional NBO analyses were also performed to qualitatively describe the chemical bonding in 0A–5A. The electrostatic interactions can be described by the natural charge distribution. As shown in Fig. 1, the N and Be atoms in 0A both possess the negative charges (−2.11 and −0.18 |e|, respectively), indicating the obvious Coulomb explosion effect, which would be the most important factor to destabilize 0A. We note that the bridging H atoms in 1A–5A all possess the negative charges (−0.21 to −0.35 |e|). Simultaneously, the natural charges on Be atoms are highly affected by the bridging H atoms. For example, the Be atoms linking one bridging H atom bear the positive charges ranging from +0.29 to +0.57 |e|, while those linking two bridging H atoms bear the charges ranging from +0.70 to +0.96 |e|. Correspondingly, for the molecular region where the Be–Be edge was bridged by an H atom, the N, Be, and H atoms possess the negative, positive, and negative charges, respectively, representing a kind of favorable Coulomb attractive interactions, which is similar to the pattern found in CBe5H3. The covalent bonding was evaluated by the Wiberg bond indices (WBIs) for selected atom interactions. We note that the bridging H atoms in 1A–5A are highly affected by the bridging H atoms.

Next, the kinetic stability of 2A–5A was studied by BOMD simulations. Fig. 5 shows the RMSD plots for a set of 100 pico-second (ps) BOMD simulations running at 4, 298, and 500 K, respectively. As the figure shows, the variation of RMSD values suggested that the structures of 2A, 3A, and 5A can be well-maintained for the simulations at all three examined temperatures, as reflected by the small RMSD values with upward jump. The RMSD plots of 4A also indicate the well-maintained structure at 4 and 298 K. However, the structure of 4A is not kinetically stable at 500 K, as mirrored by a reversible upward jump of RMSD plot at about 10 ps. The structural sampling revealed the reversible isomerization to 4C. Nevertheless, the molecules exist in the form of 4A for about 90% of simulation time, suggesting that 4A will determine the spectroscopic signals at 500 K.

Stability consideration

Table 1 The lowest vibrational frequencies (νmin, in cm−1), the Wiberg bond indices (WBIs) for selected atom–atom interactions

| WBI         | νmin (cm−1) | Be–Be       | Be–H       |
|-------------|-------------|-------------|------------|
| NBeHn+      | 218         | 0.35        | 0.17/0.94  | N/A        |
| NBeH2       | 196         | 0.32−0.44   | 0.34       | 0.43       |
| NBeH2       | 192         | 0.29−0.44   | 0.16/0.93/0.96 | 0.42/0.46 |
| NBeH3       | 167         | 0.37−0.58   | 0.15/0.17/0.96 | 0.36−0.55 |
| NBeH4       | 117         | 0.28−0.52   | 0.15/0.19/0.96 | 0.36−0.55 |
| NBeH5       | 77          | 0.42        | 0.18       | 0.46       |

be classified into two types. For Be–Be edges without H atom, the WIBIBe–Be values range from 0.93 to 0.96, pronouncing the standard single bonds. In contrast, for Be–Be edges with a H atom, the WIBIBe–Be values range from 0.15 to 0.19, suggesting the absence of direct Be–Be covalent bonding, which is consistent with the formation of H-bridged Be–H–Be 3c-2e bonds. The covalent bonding is also akin to the bonding pattern found in CBe3Hn−4 (n = 0–5).

Stability consideration

The experimental viability of a theoretically designed species is closely related to its stability. The small clusters designed in this work are expected to be realized in the gas-phase generation and characterized in the followed spectroscopy.

Since the net charges on 0A is too high to deter it from being realized experimentally, 0A was excluded during the stability studies. Herein, the thermodynamic stability of 1A–5A was examined by the extensive exploration of their PESs. At the final CCSD(T)//B3LYP level, 2A, 4A, and 5A are proved to be the GEMSs, being 0.2, 8.4, and 28.6 kcal mol−1, respectively, lower in energy than their second lowest isomers (see Fig. S3 in ESI†). As a comparison, 1A and 3A are 7.7 and 11.5 kcal mol−1 higher in energy at the same level than the located lowest-lying isomers, respectively.

Next, the kinetic stability of 2A–5A was studied by BOMD simulations. Fig. 5 shows the RMSD plots for a set of 100 pico-second (ps) BOMD simulations running at 4, 298, and 500 K, respectively. As the figure shows, the variation of RMSD values suggested that the structures of 2A, 3A, and 5A can be well-maintained for the simulations at all three examined temperatures, as reflected by the small RMSD values with upward jump. The RMSD plots of 4A also indicate the well-maintained structure at 4 and 298 K. However, the structure of 4A is not kinetically stable at 500 K, as mirrored by a reversible upward jump of RMSD plot at about 10 ps. The structural sampling revealed the reversible isomerization to 4C. Nevertheless, the molecules exist in the form of 4A for about 90% of simulation time, suggesting that 4A will determine the spectroscopic signals at 500 K.

To avoid the influence from stochastic behaviors of BOMD simulations to the conclusion of kinetic stability, we selected the 500 K as the test temperature to run additional five independent simulations for 20 ps and corresponding RMSD plots are given in ESI as Fig. S4.† As the figure shows, the structures of 2A, 3A, and 5A can also be well-maintained, while that of 4A shows the reversible instantanous upward jump. The detailed structural sampling revealed the transient existence of 4B and 4C. Nevertheless, in majority of simulation time, 4A is the main configuration, which is consistent with the above 100 ps simulation. So 4A is also kinetically viable.

Herein, we would like to compare the dynamic behaviors of ppN species NBeHn−4 (n = 2–5) with that of ppC analogue species CBe3Hn−4 (n = 2–5). Our previous studies revealed that the H atoms in CBe3Hn−3 and CBe3Hn−4 were both highly flexible, rotating around the CBe3 core moiety by moving from one Be–Be edge to another.3 However, when the ppC was replaced by
ppN, the flexibility of H atoms disappeared, as reflected by the RMSD plots of 2A and 3A without upward jump. Simultaneously, 4A and 5A inherit the good kinetic stability of CBe5H4 and CBe5H3. Therefore, the dynamic simulations not only demonstrated the good kinetic viability of 2A–5A, but also revealed that the N-substitution can fix the highly flexible H atoms found in CBe5H22− and CBe5H−.

**Stability about gaining and losing electron**

To evaluate the electron-gaining and losing properties, the VDEs and VEAs of 2A–5A were calculated. The VDE for mononion 2A is 2.52 eV, which is reasonably high for photoelectron spectroscopy, while the VEA of 2A is positive, suggesting the endothermic electron-gaining process for 2A. For neutral molecule 3A, the VDE and VEA values are 7.10 and 0.22 eV, respectively, revealing its low tendency to lose or gain an electron. For mono-cation 4A, it would be very difficult to lose an electron due to the rather high VDE of 11.93 eV and it would be not easy to gain an electron, as reflected by the VEA value (−4.41 eV) close to K+ cation (−4.34 eV). For dication 5A, it is not curious that the VDE is as high as 22.35 eV. However, its VEA value of −9.23 eV is actually very low, being lower than the VEA of Ba2+ (−10.00 eV), the lowest VEA value for any atomic dication in the Periodic Table), suggesting its relatively low tendency to gain an electron in dications. Therefore, 5A is eligible to be regarded as the so-called “superalkaline earth metal dication”, which might be stable enough to exist as the positive portion of an ionic salt.

**Conclusion**

In summary, we have demonstrated based on the extensive computational explorations that nitrogen is more suitable than carbon to fit the H-surrounded Be5 rings both geometrically and electronically. The nitrogen substitution for the planar pentacoordinate carbon in CBe5Hn+4 (n = 0–5) leads to the perfect planar structure for n = 4 and 5 and fixes the highly free H atoms for n = 2 and 3. Remarkably, when the diffused Be–Be 2c–2e σ bonds were gradually replaced by much less diffused Be–H–Be 3c–2e bonds, the structures were gradually stabilized from the electronic structure point of view, as reflected by the increasing HOMO–LUMO gaps. In six planar pentacoordinate nitrogen species designed in this work, NB5H42+ (5A) possesses the best stability, which would be promising to obtain it as the positive portion of an ionic salt.

**Conflicts of interest**

There are no conflicts to declare.

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