Received: 23 July 2020 | Revised: 2 September 2020 | Accepted: 4 September 2020

DOI: 10.1002/qua.26473

FULL PAPER

International Journal of Quantum Chemistry WILEY

Stabilization of the [cyclo-N_5]$^-$ anion by Lewis acid-base interactions

Peng Wang | Panpan Wu | Kun Wang | Longjiu Cheng

Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui, China

Correspondence
Kun Wang and Longjiu Cheng, Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, China.
Email: wangkun@ahu.edu.cn (K. W.) and clj@ustc.edu (L. C.)

Funding information
the Foundation of Distinguished Young Scientists of Anhui Province; the National Natural Science Foundation of China, Grant/Award Numbers: 21701001, 21873001

Abstract

It is an attractive problem to stabilize cyclopentazolate anion [cyclo-N_5]$^-$ due to its promising application in the field of high-energy density materials. The instability of [cyclo-N_5]$^-$ is caused by the repulsion of the neighbored lone pairs of electrons localized on N atoms. In this study, two anions of [$N_5(BH_3)_5$]$^-$ and [$N_5(AgCN)_5$]$^-$ have been designed to reduce the intramolecular repulsion. [$N_5(H_2O)_5$]$^-$ is designed to evaluate the effect of intramolecular hydrogen bond on the stabilization. For all the structures, we apply density functional theory and the *Car-Parrinello* molecular dynamics method to study the bonding properties and thermal stabilities. Based on the results, we confirm that the individual [cyclo-N_5]$^-$ anion can be effectively stabilized through coordination with acidic ligands rather than the hydrogen bond, which will provide a new method to synthesize full-nitrogen compounds.

KEYWORDS

Car-Parrinello molecular dynamics simulations, cyclopentazolate anion, density functional theory, stabilization

1 | INTRODUCTION

Stable full-nitrogen energetic materials, such as N_2, N_3^- N_4, N_5^+, [cyclo-N_5]$^-$, N_8, polymeric nitrogen, etc., attract much interest because of their extreme high-energy contents and environment-friendly products.[1–5] With the successful synthesis of complex $(N_5)_6(H_3O)_3(NH_4)_4Cl$, confirmation of the structure of cyclopentazolate anion ([cyclo-N_5]$^-$) is important because of its very broad application in the energetic area. In 2002, Vij et al. first pointed out the structure of [cyclo-N_5]$^-$ in the gas phase.[6] Haas et al. demonstrated the existence of [cyclo-N_5]$^-$ in anhydrous tetrahydrofuran (THF) solution by using liquid chromatography and mass spectrometry.[7] The enthalpy of formation of the complex containing [cyclo-N_5]$^-$ is 8000 to 20 000 kJ/kg (3-8 times 2,4,6-trinitrotoluene (TNT) equivalency).[8]

In the crystal state, there are three effective pathways to stabilize [cyclo-N_5]$^-$. First, the cross-link of hydrogen bond is a main reason to stabilize [cyclo-N_5]$^-$,[5] such as the [cyclo-N_5]$^-$ in the complex of $(N_5)_6(H_3O)_3(NH_4)_4Cl$. Second, the derivative metallic complexes or energetic ionic salts indicate that [cyclo-N_5]$^-$ can be stabilized by metal cations as well, such as $[Na(H_2O)(N_5)_2]\cdot 2H_2O$, $[TM(H_2O)_4(N_5)_2]\cdot 4H_2O$, (TM = Mn, Fe, Co, and Zn), and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$.[9–11] In addition, the energetic metal-inorganic frameworks (MIFs) are also synthesized successfully, such as $[Na(H_2O)(N_5)]\cdot {}_2H_2O$ and $[Na_8(N_5)_8(H_2O)_3]_n$.[12,13] Finally, the anhydrous and nonmetallic ionic salts are prepared, which indicates that [cyclo-N_5]$^-$ can be stabilized based on Coulomb interaction, such as 3,9-diamino-6,7-dihydro-5H-bis([1,2,4]triazolo)-[4,3-e:3′,4′g][1,2,4,5]tetrazepine-2,10-diium($(DABTT^{2+}$ $(N_5)^-{}_2$), *N*-carbamoylguanidinium ($(Gu)^+(N_5)^-$), and oxalohydrazinium pentazolate ($(Oxahy)^+(N_5)^-$).[14] It is normal to use the metal-free energetic cations to stabilize [cyclo-N_5]$^-$ to form energetic ionic salts for better energetic performances.

In the crystal phase, [cyclo-N_5]$^-$ can be stabilized by the Coulomb interactions, hydrogen bond, or coordination with metal cations.[15] Rather than stabilizing the crystal, it is an interesting problem to find the determined factor for stabilizing the individual molecular [cyclo-N_5]$^-$. Based on the Lewis acid-base theory, in order to enhance the stability of [cyclo-N_5]$^-$, an effective method is to weaken the repulsion of lone pairs on N atoms by introducing Lewis acidic ligands to combine with N atoms.

Therefore, we consider BH_3 and AgCN as two representative Lewis acids to stabilize [cyclo-N_5]$^-$, where BH_3 and AgCN are both traditional Lewis acids. BH_3 represents the traditional metal-free ligands. AgCN as a soft acid (Ag^+ is easy to be polarized) is usually utilized as a protective group for high-activity clusters. Moreover, the argentophilic interaction[16] between the neighbored molecular AgCN represents the effect of metallophilicity on the stabilization. [$N_5(H_2O)_5$]$^-$ is also designed to evaluate the effect of an intramolecular hydrogen bond on the stabilization in the anion. Based on the optimized structures, we compare their electronic structures and thermal stabilities to conclude that introducing Lewis acid to the system is the most effective pathway to stabilize the [cyclo-N_5]$^-$.

2 | COMPUTATION METHOD

We have applied four different theoretical methods and basis sets to optimize the systems, where the calculated N—N bond length (Å) has been compared with the experimental results from [cyclo-N_5]$^-$ in Table S1. Then, we confirm the results by applying the M062X/Def2TZVP[17–18] theoretical level to optimize all the structures in the GAUSSIAN 09 package.[19] To investigate the stabilities of [$N_5(BH_3)_5$]$^-$, [$N_5(AgCN)_5$]$^-$, and [$N_5(H_2O)_5$]$^-$, we calculate the binding energies between [cyclo-N_5]$^-$ and the ligands. Electrostatic potential (ESP)[20] analysis is performed to research the electron distribution. Chemical bonding analysis is carried out using the adaptive natural density partitioning (AdNDP) method.[21–33] The visualization of the molecular orbital is displayed using the MOLEKEL 5.4 package.[34] Noncovalent interaction (NCI) plots are completed by using Multiwfn[35,36] and VMD[37] packages to confirm the argentophilic interaction in [$N_5(AgCN)_5$]$^-$. The Wiberg bond index (WBI)[38] is also calculated in the Multiwfn package.

In addition, we have implemented the *Car-Parrinello* molecular dynamics (CPMD) simulation[39] to compare the initial decomposition of [cyclo-N_5]$^-$, [$N_5(BH_3)_5$]$^-$, and [$N_5(AgCN)_5$]$^-$. We build a 30 × 30 × 30 Å box for each structure to avoid the interaction between the individual anions. The total length of the simulation is about 2 ps (20 000 steps), with the fictitious electronic mass of 500 D0 based on the convergence test. Electron density cutoff energies of 40 Ry (544 eV) are set for the CPMD simulation with the Perdew-Burke-Ernzerhof function. We employed an NVT ensemble with oscillation frequencies of 550 THz[40] to control the temperature. All the CPMD simulations are performed using Quantum Espresso package 6.0.[41]

3 | RESULTS AND DISCUSSION

3.1 | Geometry structure and chemical stability

The optimized structures of [cyclo-N_5]$^-$, NH_3BH_3, [$N_5(BH_3)_5$]$^-$, [$N_5(AgCN)_5$]$^-$, and [$N_5(H_2O)_5$]$^-$ are shown in Figure 1, where NH_3BH_3 is calculated for the comparison of B—N bond under different conditions. The positive frequencies in [$N_5(BH_3)_5$]$^-$ and [$N_5(AgCN)_5$]$^-$ indicate that both the structures are the minimum points of the corresponding potential energy surfaces. [$N_5(H_2O)_5$]$^-$ is also optimized but with virtual frequencies of −23.84 cm^{-1}, indicating that H_2O cannot stabilize the individual [cyclo-N_5]$^-$ without intermolecular hydrogen bonds.

All the structures are compared, including the unstable [$N_5(H_2O)_5$]$^-$, to obtain the possible factors affecting the stability of [cyclo-N_5]$^-$. The calculated average bond distance of [cyclo-N_5]$^-$ is 1.31 Å, which is consistent with the experimental data (1.32 Å),[5] and its bond length is averaged between N—N and N═N bond, caused by the delocalization of the *p* electrons. The B—N bond length in the classic Lewis pairs of NH_3BH_3 (Figure 1) is 1.65 Å, while the B—N length in [$N_5(BH_3)_5$]$^-$ is 1.64 Å, which indicates that the interaction of the B—N bond in [$N_5(BH_3)_5$]$^-$ is stronger than that of NH_3BH_3. The average N—N bond lengths of C_1 [$N_5(BH_3)_5$]$^-$, D_{5h} [$N_5(AgCN)_5$]$^-$, and C_{5h} [$N_5(H_2O)_5$]$^-$ are all 1.30 Å at the same theoretical level.

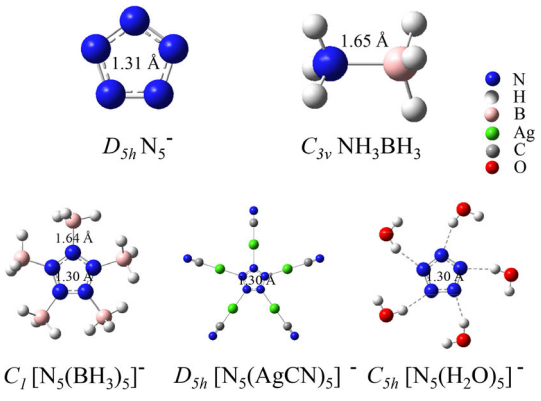


FIGURE 1 Optimized structures of [cyclo-N_5]$^-$, BH_3NH_3, [$N_5(BH_3)_5$]$^-$, [$N_5(AgCN)_5$]$^-$, and [$N_5(H_2O)_5$]$^-$

The energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) is 7.48 eV for $[N_5(BH_3)_5]^-$, 6.99 eV for $[N_5(AgCN)_5]^-$, and 11.61 eV for $[N_5(H_2O)_5]^-$. The calculated binding energy of the B—N bond of NH_3BH_3 is −44.8 kcal/mol, which is reasonable compared to the previous theoretical calculation value (−37.5 ± 3.6 kcal/mol).[42] To investigate the interaction between ligands and the anion, we studied the stabilization energies of $[cyclo\text{-}N_5]^-$ affected by different numbers of ligands in $[N_5(BH_3)_5]^-$, $[N_5(H_2O)_5]^-$, and $[N_5(AgCN)_5]^-$ on the basis of Equation (1), where all the anions are simplified as $[N_5L_n]^-$, and L and *n* indicate the ligands and the coordination number, respectively. We define the binding energy (E_b) of N-ligand as Equation (1):

$$E_b\,(\mathrm{N-ligand}) = E\,([N_5L_n]^-) - E\,([N_5L_{n-1}]^-) - E\,(L) \quad (1)$$

The relationship between the interaction of the N-ligand and the coordination number is shown in Figure 2. The results of binding energy (E_b) indicate that BH_3 and AgCN stabilize the $[cyclo\text{-}N_5]^-$ effectively because the lone-pair electrons on the $[cyclo\text{-}N_5]^-$ are shared by the Lewis acid in the coordination. As shown in Figure 2, the binding energy is very strong when the coordination number is 1 or 2 in $[N_5(BH_3)_5]^-$ and $[N_5(AgCN)_5]^-$. When the coordination number increases, the binding energy decreases significantly. As for $[N_5(H_2O)_5]^-$, the ligand of H_2O combines with the $[cyclo\text{-}N_5]^-$ by hydrogen bond through an H atom. So, the interaction between the anion and the ligands is very weak. Based on these results, $[cyclo\text{-}N_5]^-$ is stabilized mainly by the effective coordination of ligands to reduce the repulsion between the lone-pair electrons rather than the intramolecular hydrogen bonds. The binding energy of AgCN-$[N_5]^-$ is smaller than that of H_3B-$[N_5]^-$, which is caused by the strong deformability of Ag^+. It also should be noted that the argentophilic interaction hinders the strength between AgCN and $[cyclo\text{-}N_5]^-$ (as shown in Figure 3).

3.2 | Electronic structure

As for $[cyclo\text{-}N_5]^-$, all the five nitrogen atoms adopt sp^2 hybridization to form a D_{5h} symmetric conformation with a 5-center, 6-electron delocalized bond. In the meantime, the lone pair electrons localized on each nitrogen can be regarded as the active electron donor. It should be noted that the alkalinity of $[cyclo\text{-}N_5]^-$ is even stronger than that of NH_3.[43]

The ESP of $[cyclo\text{-}N_5]^-$, $[N_5(BH_3)_5]^-$, $[N_5(AgCN)_5]^-$, and $[N_5(H_2O)_5]^-$ are compared respectively in Figure 4. As plotted in Figure 4A, it is obvious that the charge is homogeneously distributed in the plane of $[cyclo\text{-}N_5]^-$, where the *p*-electrons are delocalized to form a conjugated π bond. However, the repulsion of the lone-pair electrons localized on each N atom results in the instability of $[cyclo\text{-}N_5]^-$, which can be a nucleophile with excellent activity. As show in Figure 4B-D, we notice that the charge of the ring is dispersed according to the coordination of the ligands of BH_3, AgCN and H_2O. Although the conjugacy effect of the ring is weakened by introducing the Lewis acids, the repulsion between the neighbored lone-pair electrons of $[cyclo\text{-}N_5]^-$ is decreased, which is the determined factor to stabilize the anion. Comparing (b) and (c), $[N_5(AgCN)_5]^-$ is seriously polarized because CN^- is a stronger electron-withdrawing group than that of BH_3. As for the ESP of $[N_5(H_2O)_5]^-$, the hydrogen bond is too weak to disperse the charge density of the ring, which is consistent with the corresponding results of bonding energy. Therefore, both BH_3 and AgCN are the appropriate ligands in the stabilization of $[cyclo\text{-}N_5]^-$.

On the basis of the optimized structures of $[N_5(BH_3)_5]^-$ and $[N_5(AgCN)_5]^-$, we adopt the AdNDP method to understand the relationship between the electron donors and acceptors. According to Figure 5, about 23% of the lone-pair electrons of the N atom are donated to the empty

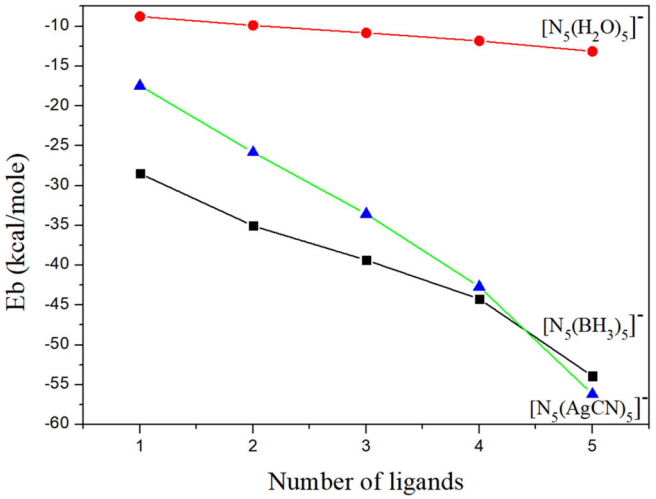


FIGURE 2 The relationship between the interaction of N-ligand and the coordination number

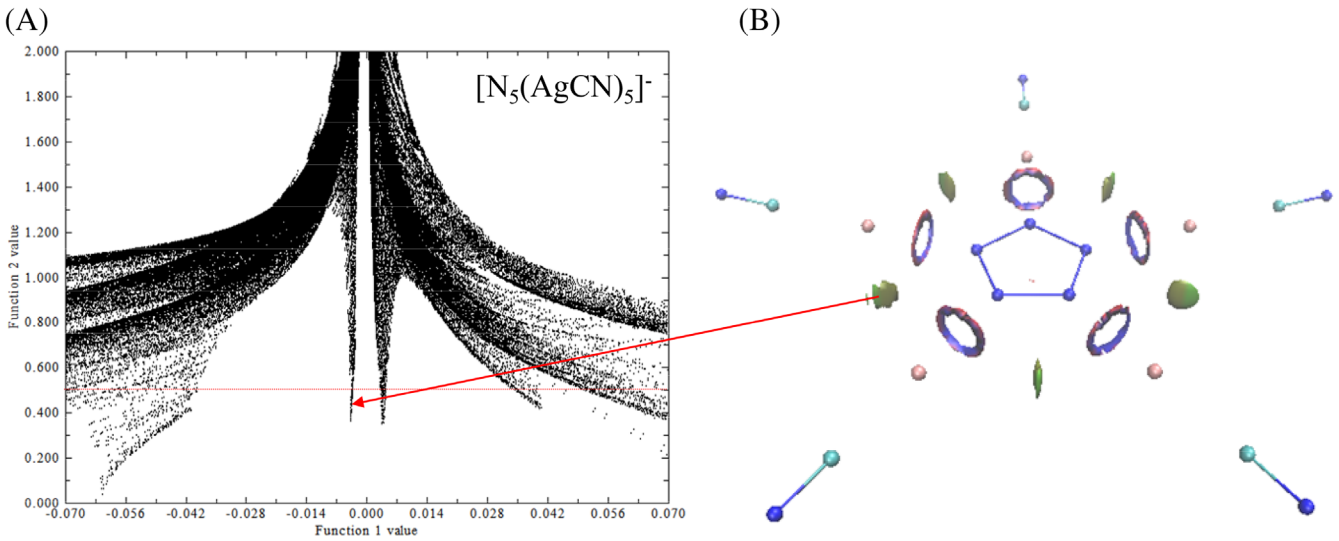


FIGURE 3 A, Plots of the reduced density gradient vs the electron density multiplied by the sign of the second Hessian eigenvalue. B, NCI isosurfaces (s = 0.50)

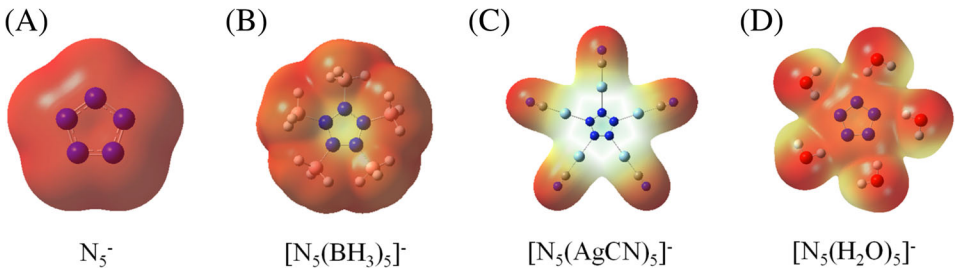


FIGURE 4 The electrostatic potential (ESP) of [cyclo-N_5]$^-$, [$N_5(BH_3)_5$]$^-$, [$N_5(AgCN)_5$]$^-$, and [$N_5(H_2O)_5$]$^-$. Red and green colors as the positive and negative potential, respectively, and the light color indicates the intermediate region

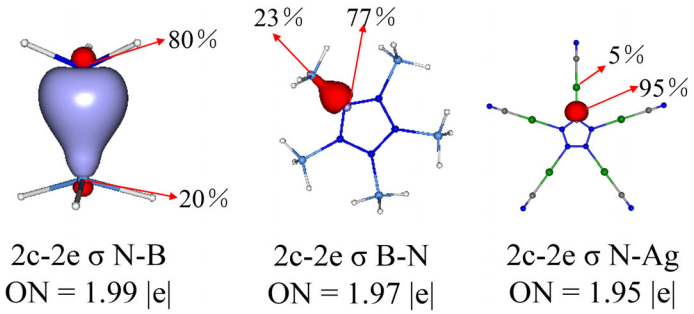


FIGURE 5 AdNDP localization for Lewis acid-base bonding in BH_3NH_3, [$N_5(BH_3)_5$]$^-$, and [$N_5(AgCN)_5$]$^-$

hybrid orbital B atom in [$N_5(BH_3)_5$]$^-$. However, for the traditional B-N bonds in BH_3NH_3, 20% of electrons is donated from the lone-pair electrons of N atoms, which are fewer than that in BH_3NH_3. As for [$N_5(AgCN)_5$]$^-$, the ratio is only 5%. (Full results of AdNDP are shown in Figures S1 and S2.) Therefore, compared with the BH_3 ligand, the proportion of electron transferring on [$N_5(AgCN)_5$]$^-$ is much smaller than that of [$N_5(BH_3)_5$]$^-$. This is because (I) Ag^+ as a soft acid is easier to be polarized than BH_3, and (II) the argentophilic interaction hinders the strength between electron donor and acceptor. Therefore, BH_3 appears to have the best performance in the stabilization. The results are consistent with that of the ESP analysis (Figure 4).

3.3 | CPMD simulation

On the basis of the energy relaxation in the NVT ensemble, we apply CPMD simulation to compare the thermal stabilities of [cyclo-N_5]$^-$, [$N_5(BH_3)_5$]$^-$, and [$N_5(AgCN)_5$]$^-$ at 700 K, where the temperature is increased to 700 K directly. The high temperature is used to accelerate the

decomposition. The simulation period is 2 ps (20 000 steps) for each structure, where the first 5000 steps are used to equilibrate the system with a changed temperature. The period is enough to compare the initial decomposition mechanisms of the three compounds.

The relationship between molecular electronic energy (a.u.) and the time of simulation (ps) is shown in Figure 6. We observe that all the structures decompose at different times at 700 K, where the initial decomposition processes of the three compounds are summarized in Scheme 1. Without the protection of BH_3 and AgCN, the ring opening of $[cyclo\text{-}N_5]^-$ is observed in the first 0.125 ps, triggered by the splitting of the N—N bond. The extensive fluctuation at around 1 ps indicates the complete decomposition of the individual anion. However, we can only find the extensive stretching vibration and splitting of B—N bond in $[N_5(BH_3)_5]^-$ or Ag—N bonds in $[N_5(AgCN)_5]^-$, rather than the ring opening of $[cyclo\text{-}N_5]^-$, indicating that both BH_3 and AgCN stabilize $[cyclo\text{-}N_5]^-$ effectively. The energy fluctuation with the same amplitude of $[N_5(BH_3)_5]^-$ or $[N_5(AgCN)_5]^-$ suggests that the $[cyclo\text{-}N_5]^-$ is protected by the ligands with no ring opening in the decomposition. In addition, we note that the vibration of the Ag—N bond is more extensive in the decomposition than that of the B—N bond (Figure 6), which is consistent with the analysis of electronic structure, where the WBI of Ag—N and B—N bonds are 0.45 and 0.95 a.u., respectively.

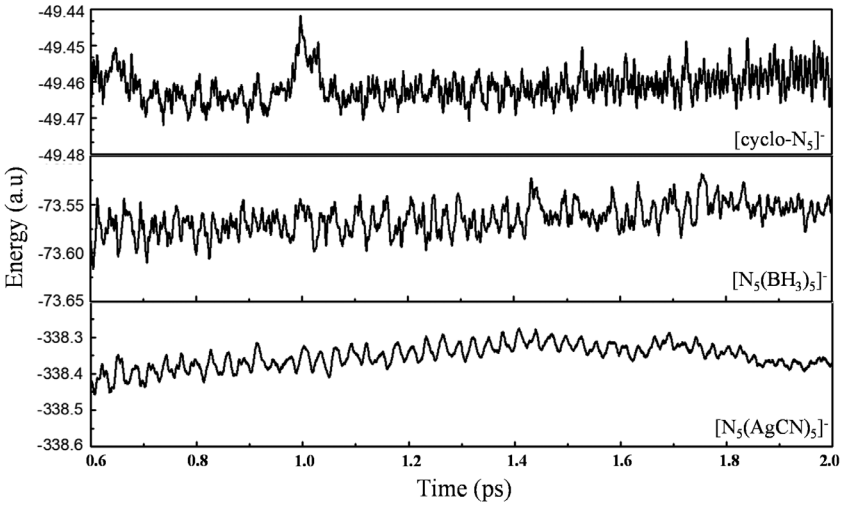
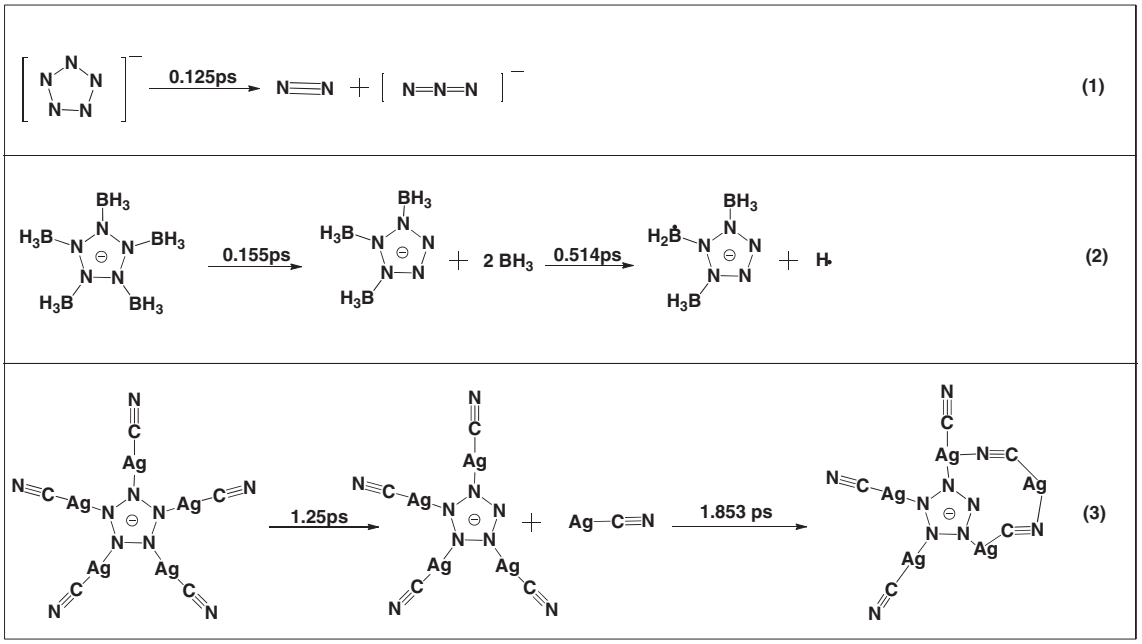


FIGURE 6 The fluctuation of total energy during *Car-Parrinello* molecular dynamics (CPMD) simulations of $[cyclo\text{-}N_5]^-$, $[N_5(BH_3)_5]^-$, and $[N_5(AgCN)_5]^-$



SCHEME 1 The initial decomposition processes of $[cyclo\text{-}N_5]^-$, $[N_5(BH_3)_5]^-$, and $[N_5(AgCN)_5]^-$ under 700 K

4 | CONCLUSION

In this work, we demonstrate a new method to stabilize the popular full-nitrogen energetic anion [cyclo-N_5]$^-$ based on the Lewis acid-base theory. Considering the effect of intramolecular hydrogen bonds and metallic ligands in the stabilization, we compare [cyclo-N_5]$^-$, [$N_5(H_2O)_5$]$^-$, [$N_5(BH_3)_5$]$^-$, and [$N_5(AgCN)_5$]$^-$, including the electronic structures, bonding properties, the interactions between ligands and anion, and the corresponding thermal stabilities at high temperature (700 K). The individual [cyclo-N_5]$^-$ is mainly stabilized by strong Lewis acids, such as BH_3 or AgCN, rather than the intramolecular hydrogen bonds or Coulomb interaction. The strategy of the stabilization of [cyclo-N_5]$^-$ is to reduce the repulsion of the neighbored lone pairs of N atoms.

Our insights into compounds with relatively high thermal stabilities under ambient conditions will guide the research and synthesis of new high-energy compounds containing [cyclo-N_5]$^-$ and help design strategies to stabilize other unstable energetic compounds.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 21873001, 21701001) and the Foundation of Distinguished Young Scientists of Anhui Province.

AUTHOR CONTRIBUTIONS

Peng Wang: Data curation; investigation. **Panpan Wu:** Investigation. **Kun Wang:** Conceptualization; investigation. **Longjiu Cheng:** Conceptualization; investigation.

ORCID

Kun Wang https://orcid.org/0000-0003-2175-1105
Longjiu Cheng https://orcid.org/0000-0001-7086-6190

REFERENCES

[1] P. C. Samartzis, A. M. Wodtke, *Int. Rev. Phys. Chem.* **2006**, *25*, 527.
[2] K. O. Christe, *Propell. Explos. Pyrot.* **2007**, *32*, 194.
[3] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem. Int. Ed.* **1999**, *38*, 2004.
[4] J. Li, K. Wang, S. Song, X. Qi, W. Zhang, M. Deng, Q. Zhang, *Sci. China Mater.* **2019**, *62*, 283.
[5] C. Zhang, C. Sun, B. Hu, C. Yu, M. Lu, *Science* **2017**, *355*, 374.
[6] A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, K. O. Christe, *Angew. Chem. Int. Ed* **2002**, *114*, 3177.
[7] B. Bazanov, U. Geiger, R. Carmieli, D. Grinstein, S. Welner, Y. Haas, *Angew. Chem. Int. Ed.* **2016**, *128*, 13427.
[8] V. Zarko, *Combust Explo Shock+* **2010**, *46*, 121.
[9] Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang, M. Lu, *Nature* **2017**, *549*, 78.
[10] C. Zhang, C. Yang, B. Hu, C. Yu, Z. Zheng, C. Sun, *Angew. Chem. Int. Ed.* **2017**, *56*, 4512.
[11] Y. Xu, P. Wang, Q. Lin, M. Lu, *Dalton Trans.* **2017**, *46*, 14088.
[12] Y. Xu, P. Wang, Q. Lin, X. Mei, M. Lu, *Dalton Trans.* **2018**, *47*, 1398.
[13] W. Zhang, K. Wang, J. Li, Z. Lin, S. Song, S. Huang, Y. Liu, F. Nie, Q. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 2592.
[14] Y. Xu, Q. Lin, P. Wang, M. Lu, *Chem. – Asian J.* **2018**, *13*, 924.
[15] P. Wang, Y. Xu, Q. Lin, M. Lu, *Chem. Soc. Rev.* **2018**, *47*, 7522.
[16] H. Schmidbaur, A. Schier, *Angew. Chem. Int. Ed.* **2015**, *54*, 746.
[17] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.
[18] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Iashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 09*, Gaussian, Inc., Wallingford, CT **2009**.
[20] C. I. Bayly, P. Cieplak, W. Cornell, P. A. Kollman, *J. Chem. Phys.* **1993**, *97*, 10269.
[21] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207.
[22] D. Y. Zubarev, A. I. Boldyrev, *J. Comput. Chem.* **2007**, *28*, 251.
[23] D. Y. Zubarev, A. I. Boldyrev, *J. Org. Chem.* **2008**, *73*, 9251.
[24] L. Cheng, Y. Yuan, X. Zhang, J. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 9035.
[25] L. Liu, P. Li, L.-F. Yuan, L. Cheng, J. Yang, *Nanoscale* **2016**, *8*, 12787.
[26] Y. Yuan, L. Cheng, *J. Chem. Phys.* **2013**, *138*, 024301.
[27] L. Li, L. Cheng, *J. Chem. Phys.* **2013**, *138*, 094312.
[28] L. Li, C. Xu, L. Cheng, *Comput. Theor. Chem.* **2013**, *1021*, 144.

[29] L. Cheng, C. Ren, X. Zhang, J. Yang, *Nanoscale* **2013**, *5*, 1475.
[30] Q. Zheng, C. Xu, X. Wu, L. Cheng, *ACS Omega* **2018**, *3*, 14423.
[31] Q. Liu, L. Cheng, *J. Alloys Compd.* **2019**, *771*, 762.
[32] Q. Liu, C. Xu, X. Wu, L. Cheng, *Nanoscale* **2019**, *11*, 13227.
[33] Y. Cui, L. Cheng, *RSC Adv.* **2017**, *7*, 49526.
[34] U. Varetto, *MOLEKEL 5.4.0.8*, Swiss National Supercomputing Centre, Manno, Switzerland **2009**.
[35] H.-P. Loock, L. M. Beaty, B. Simard, *Phys. Rev. A* **1999**, *59*, 873.
[36] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580.
[37] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics Modell.* **1996**, *14*, 33.
[38] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.
[39] R. Car, M. Parrinello, *Phys. Rev. Lett.* **1985**, *55*, 2471.
[40] S. Nosé, *J. Chem. Phys.* **1984**, *81*, 511.
[41] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *J. Phys. Condens. Matter* **2009**, *21*, 395502.
[42] J. A. Plumley, J. D. Evanseck, *J. Phys. Chem. A* **2007**, *111*, 13472.
[43] C. Jiang, L. Zhang, C. Sun, C. Zhang, C. Yang, J. Chen, B. Hu, *Science* **2018**, *359*, 8953.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Wang P, Wu P, Wang K, Cheng L. Stabilization of the [cyclo-N_5]$^-$ anion by Lewis acid-base interactions. *Int J Quantum Chem*. 2020;e26473. https://doi.org/10.1002/qua.26473