1. Introduction

In the periodic table, carbon and nitrogen are neighbors and both possess unique bonding ability to form single, double, and triple bonds, which makes them possible to form diverse molecular crystals. In fact, carbon does form rich molecular crystals, such as the fascinating family of fullerenes composed of aromatic six-membered and five-membered rings. Nitrogen is abundant in the earth and can only form molecular crystals of $N_2$ at low temperatures. Recently, the theory predicts that pure nitrogen can form chain-like $N_4$ and $N_6$ molecular crystals. However, a molecular crystal formed by an aromatic polynitrogen molecule similar to a carbon system has not been found in a full-nitrogen system, which is a great fundamental interest.

An important goal of obtaining such a molecular crystal is that the material can be used as a green, nonpolluting, high energy density material (HEDM), which not only has a very high energy density about five times that of 2,4,6-trinitrotoluene (TNT), but also has a decomposition product of only $N_2$. In fact, an aromatic pentazole ($N_5$) structure in organic compounds has been reported as early as the 1900s. In 2002, $N_5^-$ was produced in the gas phase by cleaving the $C=\text{N}$ bond in the substituted phenylpentazole. Recently, a series of solid compounds consisting of cyclic $N_5$ were synthesized under high pressure, such as $\text{CeN}_5$ and LiN$_5$[9,10]. In 2017, a breakthrough was made by successfully synthesizing such cyclic $N_5$ in five metal pentazolate hydrate complexes at ambient condition.[11,12] Since cyclic $N_5$ anion is aromatic, it has excellent stability and can be stabilized even at 100 °C. These findings in cyclo-$N_5$ anion open the door to the fascinating pentazole chemistry. However, the aromatic molecular crystal formed by the pure cyclic $N_5$ has not been reported so far.

In addition, the study of polymeric nitrogen under high pressure has also attracted great attention. Since the first polymeric nitrogen structure was proposed in 1985, a series of new structures have been designed, such as chain-like,[14–17] layer,[18,19] and 3D structures.[20–22] Experimentally, a breakthrough was made in 2004. Eremets et al.[23] observed a cg-$N$ structure from 110 to 140 GPa above 2000 K. Subsequently, Tomasino et al.[24] synthesized a new type of polymeric nitrogen called LP-N at 126–175 GPa by direct laser heating of $N_2$ in gas phase by cleaving the $C=\text{N}$ bond. However, these polymeric nitrogen structures are atomic or layered, and no aromatic molecular crystals formed by pure nitrogen have been found. Therefore, we still need...
to study whether there are aromatic molecular crystals in the nitrogen system.

Here, we predict a new form of aromatic polynitrogen crystals composed of all nitrogen \( N_{10} \) molecules from theoretical simulations. The \( N_{10} \) molecules are held together by van der Waals (vdW) interaction to form the molecular crystal and each molecule can be taken as a bispentazole molecule. This new structure has excellent stability and is metastable at ambient conditions, which is superior in energy to the previously proposed \( N_8 \) and \( N_6 \) molecular crystals. The crystal is a potential HEDM due to the high energetic \( N_{10} \) polynitrogen molecules. The prediction of such ring-like polynitrogen stable at ambient pressure may open up a new area of nitrogen chemistry to search for full-nitrogen aromatic molecular crystal and also guide the synthesis of new polymeric nitrogen.

2. Results and Discussion

Our structural search of nitrogen crystals was performed in the pressure range of 0–100 GPa by using simulation cells containing up to 40 N atoms. A new form of aromatic crystal structures composed of \( N_{10} \) molecules with space groups of P4/mmb (\( Z = 2 \)), P1 (\( Z = 3 \)), and P-1 (\( Z = 1 \)), respectively, has been obtained and all could be stable at ambient pressure. We have listed the optimized lattice parameters of three structures in Table S1 (Supporting Information). Since the \( N_{10} \) molecule has two \( N_5 \) rings, we named the molecule as bispentazole. Their structures are shown in Figure 1. Examination revealed that the P4/mmb structure consisting of two identical bispentazole molecules is the most stable phase at ambient pressure (see next), in which the bispentazole molecule with a D2d symmetry is formed by two pentazole rings (\( N_5 \)) perpendicular to each other. The bond lengths and bond energy of bispentazole molecule are shown in Tables S2 and S3 (Supporting Information). The configurations of the bispentazole molecules in the other two crystals are different, i.e., the angle between the two \( N_5 \) rings in the bispentazole molecule is between 70° and 90° in the P1 structure and is 0° in the P-1 structure (i.e., the two \( N_5 \) rings are parallel to each other). This indicates that the molecular configurations have important influence on the crystal structure and the stability of the three phases. According to these features in the corresponding molecular configurations, these three structures are named as V phase (vertical phase), I phase (inclined phase), P phase (parallel phase), respectively. Bader analysis shows that each bispentazole molecule in these structures is electrically neutral, suggesting only a weak van der Waals interaction exists between them. In addition, we take the V phase as an example to calculate the cohesive energy of the molecular crystals of \( N_{10} \). The calculated results show that the cohesive energy of the crystal of the molecule is 48.8 kJ mol\(^{-1}\) (11.6 kcal mol\(^{-1}\)). This cohesive energy is significantly higher than the cohesive energy of \( \alpha \)-phase of \( N_2 \) due to the strong electrostatic interaction between the \( N_{10} \) molecules, similar to the previously reported \( N_8 \) molecules\(^4\) as well as \( CO_2\)\(^2,25\) and acetonitrile\(^2,26\). Moreover, we calculate the cohesive energy without vdW interaction, which is 10.0 kJ mol\(^{-1}\) (2.4 kcal mol\(^{-1}\)). It is clearly shown that the cohesive energy of the \( N_{10} \) molecular crystal with vdW interaction is increased by almost four times than that without vdW interaction. This result indicates that vdW interaction plays an important role in the stability of the system.

The enthalpies of the three molecular crystal structures together with other known structures are plotted as a function of pressure in Figure 2. We introduced the van der Waals interaction by using the DFT-D2 method. The results show that our three structures have much lower energy at low pressure compared to the well-studied \( cg-N \). At ambient pressure, among the three newly proposed structures, the energy of V phase is the lowest and P phase is the highest, while I phase in the middle. As pressure gradually increases, I phase structure becomes the most stable with the lowest energy above 1.6 GPa; at pressure higher than 2.5 GPa, the energy of the P phase becomes the lowest, as shown in Figure 2b. It is worth noting that all these three crystals have lower energy than \( cg-N \) at pressure below 39.3 GPa, and lower energy than \( \varepsilon-N_2 \) above 59.0 GPa. Moreover, the three crystal structures also exhibit lower energy over the entire pressure range than the previously reported \( N_8 \)\(^4\) and \( N_6 \)\(^5\) molecular crystals. Note that both \( cg-N \) and \( N_8 \) structures have been successfully synthesized in experiment, while \( N_5 \) ring has also been recently identified in cyclo-N\(_2\)-based complexes. Therefore, it is very promising to synthesize the \( N_{10} \) molecular crystals proposed here in experiment. We also calculated the X-ray diffraction patterns and vibrational spectra of the V phase for future experimental reference (Figures S1 and S2, Supporting Information).

**Figure 1.** a–c) Energetically favorable structures of V phase, I phase, and P phase, respectively, according to the molecular configurations of the building blocks.
Cyclic $N_5^-$ is a potential candidate for full-nitrogen energetic materials and can be isolated only from acidic solution. Recent researches\(^{27,28}\) reported the stability and energy storage mechanism of the cyclic $N_5^-$ in acidic solution, namely, the resultant force of the circumferential $H\leftrightarrow H$ repulsion stretches the $N:H\leftrightarrow O$ bond to lengthen the $N:H$ and shortens the $H:O$, which weakens the $N:O$ repulsion and shortens the $N\rightarrow N$ bond along the cyclo-$N_5^-$, thereby making the internal energy of the system store energy; the $N:O$ repulsion destroys or reduces the aromaticity of cyclo-$N_5^-$ and makes cyclo-$N_5^-$ unstable, while the strong acidic solution recombines or enhances the aromaticity of cyclo-$N_5^-$ and stabilizes cyclo-$N_5^-$, making cyclo-$N_5^-$ stable only in sufficiently acidic conditions. Similar to the effect of $H\leftrightarrow H$ repulsion stretching (acidic solution) in references, the pressure here plays a significant role for both energy storage and stability of $N_{10}$ molecular crystal. In order to further analyze the stability and energy storage mechanism of $N_{10}$ molecular crystal, we take the pressure as an example for the following discussion. As shown in Figure S3 (Supporting Information), we show the orientation of each $N_{10}$ molecule in the $V$ phase. We calculate the Shannon aromaticity (SA) that is used to characterize the aromaticity, the distance between $N_{10}$ molecules on different pressures, as shown in Table S3 (Supporting Information). By comparing the SA under different pressure, we find that with the increasing of pressure, the aromaticity of $N_{10}$ molecule increases gradually increased with the decrease of SA value, which also shows that the stability of $N_{10}$ molecules is gradually increased. By comparing the intermolecular distances and the intramolecular bond lengths under different pressure, we find that the intermolecular distances of $N_{10}$ molecules and lengths of $N\rightarrow N$ bond in $N_{10}$ molecule appear to shorten gradually with the increase of pressure, which is, with the increase of the intermolecular repulsion force, the lone pairs of electrons extend radially away from each molecule, weakening the circumferential repulsion between the lone pair of electrons and shortening all $N\rightarrow N$ bonds in the $N_{10}$ molecule, and thus enhance all $N\rightarrow N$ bonds by $\approx 26.3$ kcal mol$^{-1}$ at 25.0 GPa. Therefore, high pressure plays a significant role for both energy storage and stability of $N_{10}$ molecular crystal.

To understand the configuration-dependent systematic energy variation of the three structures, we calculate the energy of a bispentazole molecule (i.e., building block) with varying the angle between the two $N_5$ rings in the molecule (Figure 3a). The results are shown in Figure 3b. It can be seen that at ambient pressure, the bispentazole molecule with the two $N_5$ rings parallel to each other (P-configuration) has the highest systematic energy; its energy gradually decreases as the angle increases (I-configuration) and reaches the lowest energy when the two $N_5$ rings are perpendicular to each other (V-configuration). This is also consistent with previous literatures\(^{29}\), confirming that the vertical bispentazole molecule has the lowest energy in all $N_{10}$ isomers. This also explains why V phase has the lowest energy at ambient pressure and P phase has the highest energy. In addition, as the pressure increases, the structural transitions from V phase to I phase and then to P phase can also be explained by the molecular configurations in the three phases, i.e., at ambient pressure, the bispentazole molecule with V-configuration needs to occupy the largest volume and possess the lowest energy; with pressure increasing, the bispentazole molecule tends to have V-configurations, causing the increase of the structural energy; at higher pressure, the bispentazole molecule forms P-configuration and the systematic energy is increased to the maximum.

Furthermore, we calculated the phonon spectra of V phase at 0 GPa, I phase at 2 GPa, and P phase at 20 GPa, respectively, to confirm the dynamic stability of their molecular crystals. The results are shown in Figure 4. It can be seen that all the three structures have no imaginary frequency under the corresponding pressure, indicating that these structures are dynamically stable. It is worthy to mention that no imaginary frequency is found in the phonon spectra of I phase and P phase at 0 GPa, suggesting that V, I, and P phases all can be metastable at ambient pressure.

The electronic properties of the bispentazole molecular crystals have been further calculated by using the Perdew, Burke, and Ernzerhof (PBE) and the Heyd, Scuseria, and Ernzerhof...
(HSE) method, including the band structure, the partial densities of states (PDOS), and the electronic local functions (ELFs), as shown in Figure 5. Take the V phase as an example, our calculation shows that it is an insulator with an indirect bandgap of 4.2 eV at the PBE level. Note that it is commonly accepted that the HSE method is one of the most accurate methods for band structure calculation while the PBE method usually underestimates the bandgap of the structure. Therefore, we have recalculated the band structure of the V phase, and the bandgap at 0 GPa is 6.1 eV at the HSE level (Figure S4, Supporting Information). Analysis of ELFs and partial densities of states suggests that the N atoms in N₅ rings are sp² hybridized with lone pair lobes pointing at the edge of the N₅ ring, whereas the bridge N atoms bonding two N₅ rings are sp² hybridization with lone pair pₓ at both sides of the bridge N. In each N₅ ring of the N₁₀ molecule, the bridge nitrogen atom provides two pₓ orbits, and the other nitrogen atoms provide one pₓ orbit, and a total of six electrons form a delocalized π bond. Therefore, the N₁₀ molecule retains the aromaticity, which also makes it have lower energy and higher stability. In addition, our calculation of the electronic properties of the I and P phases also suggest their insulating features, and the bonding type in the corresponding bispentazole molecules is the same as that of V phase (Figures S5 and S6, Supporting Information).

The thermal stability of V phase has been evaluated by using a supercell with 160 nitrogen atoms as a model, which is carried out by ab initio molecular dynamics (AIMD) simulations from 300 to 3000 K with a step size of 100 K. Snapshots of V phase structure taken at the end of 20 ps simulations are presented in Figure 6. The framework of each bispentazole

---

Figure 3. a) N₁₀ molecule configurations with different rotation angles. b) Total energies as a function of N₅ orientation at ambient pressure of N₁₀.

Figure 4. a–c) Phonon spectrum of V phase at 0 GPa, I phase at 2 GPa, and P phase at 20 GPa, respectively.
molecule is stable up to 500 K after 20 ps dynamical simulation. As the temperature increases about 600 K, one of N_5 rings in the bispentazolate molecule is opened and the bispentazolate molecule is decomposed into azidopentazole (N_8) and N_2 molecules. Note that the decomposed N_8 can be taken as a molecule formed by bonding a N_5 to an azide-like N_3 ion. It also indicates that the bispentazolate should have enough kinetic energy to cross the barrier and turn to be corrupt at the temperatures between 500 and 600 K. As the temperature increases, more bispentazolate molecules decompose into N_8 and N_2, and they completely decompose above 1500 K. Further increasing the temperature leads to the decomposition of the generated N_8 into N_6 and N_2 molecules, in which the generated N_6 molecule has a chain-like configuration identical to that

Figure 5. a) Band structure and PDOS; b) The calculated ELF isosurface of V phase at ELF = 0.83.

Figure 6. The snapshots at 500, 600, 800, 1200, 1500, 2000, 2500, and 3000 K after 20 ps in the MD simulations.
reported in previous literature.[5] At temperatures above 2600 K, the decomposition product is only N₂ molecules. Furthermore, we investigate the decomposition pathway of this N₁₀ molecule by using climbing image nudged-elastic band (CI-NEB) method. Our calculations show that the transition barriers of the three decomposition processes are 10.1 mol⁻¹ for TS₁ [N₁₀ → TS₁ → N₈ + N₂], 12.0 mol⁻¹ for TS₂ [N₈ → TS₂ → N₆ + N₂], and 19.4 kcal mol⁻¹ for TS₃ [N₆ → TS₃ → 3N₂] (Figure S7, Supporting Information). The calculated results show that TS₁ has a smaller reaction energy barrier, and TS₂ and TS₃ have relatively larger reaction energy barriers, which correspond to the lower decomposition temperature of N₁₀ and the higher decomposition temperature of N₈ and N₆ in AIMD simulations. In addition, decomposition of N₁₀ molecules into N₂ molecules can release energy of 192.0 kcal mol⁻¹ during this process.

The total energy calculation shows that V phase can release energy of 15.8 eV/cell under ambient pressure, corresponding to an energy density of about 5.5 kJ g⁻¹. This is much higher than those typical energetic materials, such as TATB, RDX, and HMX, which have energy densities around 1–3 kJ g⁻¹. In addition, due to the instability of a single cyclic N₅ ring, non-energetic ions are required to stabilize them in the complexes in previous works,[9–12,31,32] which reduces the energy density of the materials. In our predicted three polynitrogen crystals, the covalent bond between the two cyclic N₅ rings naturally stabilize each other and thus form stable bispentazole molecular crystals even at ambient pressure. Since no impurity ions are introduced in our systems, this class of all-polynitrogen crystal has a higher energy density and thus promises for a high energy density material. Our results also indicate that, compared with the polynitrogen system with chain-like configuration, such as N₈ and N₆, ring-like aromatic polynitrogen might be more stable building blocks for nitrogen allotropes in some structures that can be stable at ambient pressure, as the well-known C₆₀ in carbon allotropes. The existence of stable nitrogen crystals composed of all-cyclic N₅ may also guide the synthesis of a fully cyclic N₅ system in experiment.

In summary, we have predicted a form of new all-nitrogen aromatic molecular crystals, named as V, I, P phase, which are a type of N₁₀ molecule formed by two five-membered cyclic configuration units bonded to each other. The calculated phonon spectra indicate that crystal structures are metastable under ambient pressure, indicating that these structures have the possibility of synthesis in experiment. First-principles molecular dynamics calculations show that the structures can exist stably at room temperature, and even to 500 K. The bispentazole molecule proposed here makes two N₅ polynitrogen rings stable without introducing any impurity ions, which contains a high energy density and is therefore a potential high energy density material. These structures represent one possible way to synthesize a full-nitrogen aromatic molecular crystal.

3. Experimental Section

The CALYPSO code[33,34] was used for structural search, and the underlying structural relaxation by using the Vienna Ab initio Simulation Package (VASP).[35] The projector augmented wave (PAW) method to represent ion–electron interactions and the generalized gradient approximation (GGA) of the form proposed by PBE[36] as the electron exchange correlation functional were used. In order to achieve excellent convergence of the total energy, the cutoff value of the plane wave was set to 900 eV. The Monkhorst–Pack method was used to sample the Brillouin zone for geometric optimization and self-consistent calculations. To determine the kinetic stability of the molecular crystal structure, the PHONOPY code[37] is used for phonon dispersion analysis. An AIMD simulation of 20 ps was performed to evaluate the thermal stability of all molecular crystals. CI-NEB method[38,39] within VASP was used to find the minimum energy paths and the transition states for diffusion of N₁₀ molecule. Covalent bond energies were calculated by the integrated value of crystal orbital Hamilton population (COHP) at the band energy using the HASEM package.[40,41]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

S.L. and L.Z. contributed equally to this work. The authors sincerely thank Prof. Yanning Ma for providing the Crystal structure AnalyLysis by Particle Swarm Optimization (CALYPSO) code, and Dr. Lei Zhang, Shengli Jiang, Guoling Li, Zhaowu Wang, and Zhenlong Lv for helpful discussions. This work was financially supported by the National Key R&D Program of China (No. 2018YFA0303900), National Natural Science Foundation of China (Nos. 11847094, 11634004, and 11604116), and JLU Science and Technology Innovative Research Team (No. 2017TD-01).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

high energy density materials, molecular crystals, N₁₀ molecule, polynitrogen

Received: August 29, 2019
Revised: February 11, 2020
Published online: March 30, 2020

[1] H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl, R. E. Smalley, Nature 1985, 318, 162.
[2] F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, A. Koch, Science 1991, 252, 548.
[3] K. Balasubramanian, J. Phys. Chem. 1995, 99, 6509.
[4] B. Hirshberg, R. B. Gerber, A. I. Klymov, Nat. Chem. 2014, 6, 52.
[5] M. J. Greschner, M. Zhang, A. Majumdar, H. Liu, F. Peng, J. S. Tse, Y. Yao, J. Phys. Chem. A 2016, 120, 2920.
[6] M. I. Erements, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, R. Boehler, Nat. Mater. 2004, 3, 558.
[7] T. Curtius, A. Darapsky, E. Müller, Ber. Dtsch. Chem. Ges. 1915, 48, 1614.
[8] A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, K. O. Christe, Angew. Chem., Int. Ed. 2002, 41, 3051.
[9] B. A. Steele, E. Stavrou, J. C. Crowhurst, J. M. Zaug, V. B. Prakapenka, I. I. Oleynik, Chem. Mater. 2017, 29, 735.
[10] D. Laniel, G. Weck, G. Gaiffe, G. Garbarino, P. Loubeyre, J. Phys. Chem. Lett. 2018, 9, 1600.
[11] C. Zhang, C. Sun, B. Hu, C. Yu, M. Lu, Science 2017, 355, 374.
[12] Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang, M. Lu, Nature 2017, 549, 78.
[13] A. K. McMahan, R. LeSar, Phys. Rev. Lett. 1985, 54, 1929.
[14] W. D. Mattson, D. Sanchez-Portal, S. Chiesa, R. M. Martin, Phys. Rev. Lett. 2004, 93, 125501.
[15] M. M. G. Alemany, J. L. Martins, Phys. Rev. B 2003, 68, 024110.
[16] R. M. Martin, R. J. Needs, Phys. Rev. B 1986, 34, 5082.
[17] S. P. Lewis, M. L. Cohen, Phys. Rev. B 1992, 46, 11117.
[18] F. Zahariev, A. Hu, J. Hooper, F. Zhang, T. Woo, Phys. Rev. B 2005, 72, 214108.
[19] Y. Ma, A. R. Oganov, Z. Li, Y. Xie, J. Kotakoski, Phys. Rev. Lett. 2009, 102, 065501.
[20] C. Mailhiot, L. Yang, A. K. McMahan, Phys. Rev. B 1992, 46, 14419.
[21] X. Wang, Y. Wang, M. Miao, X. Zhong, J. Lv, T. Cui, Y. Ma, Phys. Rev. Lett. 2012, 109, 175502.
[22] F. Zahariev, S. V. Dudiy, J. Hooper, F. Zhang, T. K. Woo, Phys. Rev. Lett. 2006, 97, 155503.
[23] D. Tomasino, M. Kim, J. Smith, C. S. Yoo, Phys. Rev. Lett. 2014, 113, 205502.
[24] D. Laniel, G. Geneste, G. Weck, M. Mezouar, P. Loubeyre, Phys. Rev. Lett. 2019, 122, 066001.
[25] R. Lesar, R. G. Gordon, J. Chem. Phys. 1983, 78, 4991.
[26] A. Olejniczak, A. Katrusiak, J. Phys. Chem. B 2008, 112, 7183.
[27] L. Zhang, C. Yao, Y. Yu, S.-L. Jiang, C. Q. Sun, J. Chen, J. Phys. Chem. Lett. 2019, 10, 2378.
[28] C. Jiang, L. Zhang, C. Sun, C. Zhang, C. Yang, J. Chen, B. Hu, Science 2018, 359, 8953.
[29] L. J. Wang, P. G. Mezey, M. Z. Zgierski, Chem. Phys. Lett. 2004, 391, 338.
[30] W. J. Evans, M. J. Lipp, C. S. Yoo, H. Cynn, J. L. Herberg, R. S. Maxwell, M. F. Nicol, Chem. Mater. 2006, 18, 2520.
[31] C. Sun, C. Zhang, C. Jiang, C. Yang, Y. Du, Y. Zhao, K. O. Christe, Nat. Commun. 2018, 9, 1269.
[32] Y. Xu, Q. Lin, P. Wang, M. Lu, Chem. - Asian J. 2018, 13, 924.
[33] Y. Wang, J. Lv, L. Zhu, Y. Ma, Phys. Rev. B 2010, 82, 094116.
[34] Y. Wang, J. Lv, L. Zhu, Y. Ma, Comput. Phys. Commun. 2012, 183, 2063.
[35] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.
[36] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
[37] A. Togo, F. Oba, I. Tanaka, Phys. Rev. B 2008, 78, 134106.
[38] G. H. J. Henkelman, H. Jónsson, J. Chem. Phys. 2000, 113, 9978.
[39] G. H. J. Henkelman, B. P. Uberuaga, H. Jónsson, J. Chem. Phys. 2000, 113, 9901.
[40] L. Zhang, S.-L. Jiang, Y. Yu, Y. Long, H.-Y. Zhao, L.-J. Peng, J. Chen, J. Phys. Chem. B 2016, 120, 11510.
[41] H. Li, L. Zhang, N. Petrutik, K. Wang, Q. Ma, D. Shem-Tov, F. Zhao, M. Gozin, ACS Cent. Sci. 2020, 6, 54.