Crystalline Structures and Energetic Properties of Lithium Pentazolate under Ambient Conditions

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ABSTRACT: Recently, it has been reported that high-pressure synthesized lithium pentazolates could be quenched down to ambient conditions. However, the crystalline structures of LiN₅ under ambient conditions are still ambiguous. In this work, the structures of LiN₅ compound were directly explored at atmospheric pressure by using a new constrain structure search method. By using this method, three new allotropes were confirmed, and they show lower energy than the previous reported LiN₅ phases. Both their thermodynamic and dynamic stability were confirmed through formation enthalpies, phonon spectrum, and ab initio molecular dynamics simulations under ambient conditions. Moreover, these three allotropes show similar formation enthalpies and properties, which suggests that it is hard to obtain a single LiN₅ phase, which is well consistent with the experimental phenomenon. Furthermore, because of their low formation energy, all of them possess low energy density when they directly decompose to Li₂N and nitrogen (0.52 kJ/g). Instead, the decomposed energy could be further improved to 3.78 kJ/g when they decompose under an oxygen-rich environment.

1. INTRODUCTION

Pentazolate anion (cyclo-N₅⁻) is receiving ever-increasing significant interest because of its potential application in high-energy density materials.¹⁻⁸ Especially, since 2016, several breakthroughs have been witnessed in this field, including some metal-free pentazolate hydrates [such as (N₅)₄(H₂O)₃−, (NH₄)₄Cl salt] and metal salts [such as [Na(H₂O)(N₅)₂]·2H₂O, [Mn(H₂O)₄(N₅)₂]·4H₂O and [Mg(H₂O)₄(N₅)₂]·4H₂O] synthesized in experimentation under ambient conditions.¹⁰⁻²¹ However, the nonenergetic group (such as water and halogen) lowers the nitrogen concentration as well as energy density of these compounds.¹⁸⁻²² One important way to obtain nonenergetic group metal pentazolates (such as CsN₅, NaN₅) is by using high pressure and laser-heating, but few of them could be quenched down to ambient. In 2015, Peng et al. and Shen et al. independently predicted that LiN₅ could be synthesized under high pressure (15−100 GPa) through theoretical prediction,²³,²⁴ and Laniel et al. successfully achieved this goal by the experiment method at 2018.²⁵ Moreover, the synthesized compounds could remain stable when releasing pressure to ambient conditions. These reports are important for synthesizing and applying polynitrogen materials under atmospheric pressure. However, Laniel et al. could not obtain a single clean diffraction pattern containing solely the diffraction lines despite many attempts, and the crystalline structure of the LiN₅ compound is still unclear.²⁵

There are series of excellent reports that worked on predicting metal pentazolates, which usually can become thermodynamically stable under high pressure, such as CuN₅, LiN₅, NaN₅, ZnN₁₀, and AlN₁₅.²₅⁻₃⁵ However, these predictions are hard to be directly applied to the ambient conditions, which require to directly search metastable structures. Notably, it is still a big challenge to directly find the most stable microstructures of metal pentazolate compounds by the pristine structure search algorithm because N₅ molecules have much more selective advantages than the N₅ ring in energy. Also, the structures were obtained from high-pressure search, and there is no guarantee that they have the lowest energy at atmospheric pressure and very often they do not.²₄,²³ Recently, we have overcome this difficulty by proposing a constrained crystal structure search method to directly predict the most stable MgN₁₀, AlN₁₅, and CuN₅ crystalline structure and property under ambient conditions.³₃⁻₃⁵ Although there are some theoretical reports on the structures of LiN₅ compounds among 15−100 GPa, but the most stable phase structures still are not confirmed between 0 and 15 GPa. Hence, several basic questions are still in urgent need to be answered: (1) what is the most stable crystalline structure of LiN₅ under atmospheric pressure? (2) How about
their stability and energetic property? (3) Why can these compounds be stable under ambient conditions?

In this work, to answer the above questions, the constrained crystal structure search method was used to explore the crystalline structures between 0 and 15 GPa. Here, three possible new allotropes of LiN₅ under the ambient condition were reported, and the structure phases between 0 and 15 GPa were confirmed in this work. Moreover, the stabilities of these structure phases were evaluated by formation enthalpies, phonon spectrum, and ab initio molecular dynamics (AIMD) simulations. These structures have a great possibility to coexist at a certain low pressure because they have very close formation enthalpy and similar properties, which could be used to explain that why Laniel et al. could not obtain solely the diffraction lines of the LiN₅ compounds. Furthermore, these compounds show low energy density (about 0.53 kJ/g) when directly decompose to Li₄N and N₂. An alternative approach is to make LiN₅ decomposing under an oxygen-rich environment, and the energy density would improve to 3.78 kJ/g.

2. CALCULATIONAL METHODS

The structure predictions were through a global minimization of potential energy surfaces based on the particle swarm optimization methodology as implemented in the CALYPSO code. The stoichiometric (LiN₅)ₓ (x = 2–6) up to 3000 structures were directly searched in our simulations under 1 atm. The cyclo-N₅⁻ was constrained as a group unit to produce initial structures, and all the structures were optimized by the local density functional theory (DFT) soft package until converged. Also, then, structures were ranked according to their enthalpy, and the top 50 structures were further optimized with finer convergence criteria and used for further stability analysis.

The local structural relaxations and electronic properties calculations were performed in the framework of DFT as implemented in the Vienna Ab initio Simulation Package (VASP) by directly decomposing with the reaction of 3 Li₃N + 7 N₂ to LiN₅. Also, under an oxygen-rich environment, with the reaction of 4 Li₃N + O₂ → 2 Li₂O + 10 N₂ was used to calculate the E_d by using the following formula

\[ E_d = [3H_{LiN_5} - H_{Li_3N} - 7H_{N_2}] / [3M_{LiN_5}] \]

in which energy H is obtained for the thermodynamically stable structures of certain compositions at each given pressure. For pure N₂, Pn3m-phase, P42/mmcm-phase, and P2₁/c-phase nitrogen crystal were considered. For pure Li, the bcc-phase, fcc-phase, c16-phase, and A2b-40-phase were considered. The decomposed energy (E_d) of LiN₅ compounds was evaluated by directly decomposing with the reaction of 3 LiN₅ → Li₄N + 7 N₂ by using the following formula

\[ E_d = [4H_{LiN_5} - H_{2Li_2O} - 2H_{Li_4N} - 10H_{N_2}] / [4M_{LiN_5}] \]

3. RESULTS AND DISCUSSION

3.1. Formation Enthalpy and Energy Density. After thousands of times calculations and data screening, we get three new LiN₅ allotropes, whose formation enthalpies are both negative at 1 atm. Their space groups are P6₃22, P2₁, 2₁2₁, and Pnna, so they were named P6₃22-LiN₅, P2₁-LiN₅, and Pnna-LiN₅, respectively. As shown in Figure 1a, we listed the formation enthalpies of these seven LiN₅ allotropes, including three new phases and four have already reported phases (obtained from high pressure) (named P2₁-LiN₅, P2₁/m-LiN₅, P2₁/c-LiN₅, and C2c-LiN₅) in the pressure range of 0–15 GPa. Notably, the four allotropes, including P6₃22-LiN₅, P2₁, 2₁2₁-LiN₅, Pnna-LiN₅, and P2₁/c-LiN₅ are more stable than the others because they have negative formation enthalpy at 1 atm (shown in Table 1). If ignoring the kinetic barrier, they

\[ H_f = \frac{(2H_{LiN_5} - 2H_{Li_4N} - 5H_{N_2})}{12} \]
show great possibility to be formed when their high-pressure-synthesized compounds were released pressure to ambient conditions. In particular, the formation enthalpy curve of P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5} decreases very slowly when compared to other allotropes, which indicate that P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5} is harder to directly form under high pressure. Furthermore, the formation enthalpy curve of P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5} and P2\textsubscript{1}/c-LiN\textsubscript{5} is very close at 0–15 GPa (smaller than 0.07 eV/atom), and these two phases are with great possibility to coexist at low pressure that might be used to explain why Laniel et al. could not obtain solely the di-LiN\textsubscript{5}.

Also, the formation enthalpies at higher pressure of up to 100 GPa of these seven allotropes are listed in Figure S2, and as shown in Table S1. We can directly see the remarkable contradiction between high energy density and high stability, which include 
P2\textsubscript{1}/c-LiN\textsubscript{5}, and P2\textsubscript{1}/c-LiN\textsubscript{5}, because they have great possibility to maintain stability at ambient conditions. The lattice constant and Wyckoff positions of them are shown in Table S1. As shown in Figure 2a, P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5} presents a hexagonal symmetry, each Li forms five bonds with the \(\eta^5\)-N\textsubscript{5} ring, and a half octahedral configuration around the Li atom is presented in the structure. The bond lengths of N–N are both about 1.32–1.33 Å, which is close to the typical N–N bond length of cyclo-N\textsubscript{5} in [Mn-(H\textsubscript{2}O)\textsubscript{4}(N\textsubscript{2}H\textsubscript{4})\textsubscript{2}]-4H\textsubscript{2}O, and the nearly equal bond length indicates the good aromatic properties of cyclo-N\textsubscript{5} in P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5}. Also, there are three type Li–N bonds, including the length of 2.31, 2.10, and 2.14 Å (Figure 2a), which is a bit larger than the average bond length (2.11 Å) of Li–N in P6\textsubscript{2}/mmc-LiN.

For P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5}, and P2\textsubscript{1}/c-LiN\textsubscript{5}, they are all composed of the tetrahedral Li configuration unit, and each Li forms four bonds with the \(\eta^3\)-N\textsubscript{5} ring. Also, they just show different space groups. As shown in Figure 2b–d, the P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5} and P2\textsubscript{1}/c-LiN\textsubscript{5} present a rectangular block lattice, and P2\textsubscript{1}/c-LiN\textsubscript{5} shows a monoclinic lattice. The bond lengths of N–N in P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5}, P2\textsubscript{1}/c-LiN\textsubscript{5}, and Pnac-LiN\textsubscript{5} compounds are all about 1.32–1.33 Å, which are close to the P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5} phase, indicating good aromaticity in cyclo-N\textsubscript{5}. The bond length of Li–N in P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5}, P2\textsubscript{1}/c-LiN\textsubscript{5}, and Pnac-LiN\textsubscript{5} phase is all about 2.10 Å, which is a bit smaller than the P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5} phase. Hence, the similar coordination unit and bond length could

### Table 1. Formation Enthalpy at 1 atm and Decomposing Energy Density with and without Oxidant

| name                                      | P6\textsubscript{2}2\textsubscript{2} | P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} | Pnac | P2\textsubscript{1}/c | P2\textsubscript{1}/m | C2c |
|-------------------------------------------|-------------------------------------|---------------------------------|--------|------------------------|-------------------------|--------|
| formation enthalpy at 1 atm (eV/unit)     | −0.13                               | −0.05                           | −0.05  | −0.06                  | 0.38                     | 0.57   |
| decomposed energy without oxidant (kJ/g)  | 0.52                                | 0.61                            | 0.61   | 0.61                   | 1.15                     | 1.38   |
| decomposed energy with oxidant (kJ/g)     | 3.68                                | 3.78                            | 3.78   | 3.78                   | 4.31                     | 4.55   |

Figure 2. Unit cell of the (a) P6\textsubscript{2}2\textsubscript{2}-LiN\textsubscript{5}, (b) P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}-LiN\textsubscript{5}, (c) P2\textsubscript{1}/c-LiN\textsubscript{5}, and (d) Pnac-LiN\textsubscript{5} at 1 atm. Half octahedral and tetrahedral Li coordination units are composed of the compounds.
result in very close formation enthalpy between these three phases at ambient conditions. Suffering from less coordination number, these three phases have a bit higher formation enthalpy (0.072 eV/atom) than P$_6$122-LiN$_5$, and these three phases show more homogeneous bonding features, which increases their possibility of coexisting at ambient conditions.

3.3. Stability Evaluations. Furthermore, the stabilities of these allotropes were evaluated by dynamic and thermodynamic
3.4. Bonding Analysis. Electron localization function (ELF) is a measurement of the possibility to detect an electron at a given spatial point. In Figure 5a–d, the red area is close to 1.0 probability to detect electrons while the blue area is 0 possibility to find electrons. ELF was used to evaluate the bond property and strength of Li–N bond, and Figure 5a–d clearly shows that the localized electrons are between N and N atoms and between Li and N atoms in all LiN5 allotropes, indicating that there might form a strong covalent bond between N and N atom in cyclo-N5−, and Li atoms form coordinate bonds with the lone pair electrons of N atoms.

The charge information on each atom was further calculated by Bader’s quantum theory of atoms in molecules50,51 and is shown in Figure 5e–h, and we can see that the Li atoms play a role of the electron-donating unit, and each Li atom loses about 0.86 electrons to cyclo-N5− and shows +1 valence state. The charge distribution on cyclo-N5− is more homogeneous (0.10–0.20) than many known pentazolates (Figure S4), which reveals good aromaticity in these compounds. Especially in P6322-LiN5, each Li atom has five coordination number, every N atom in cyclo-N5− is coordinated with the Li atom, and the electrons on the N atom in cyclo-N5− are roughly equal, which caused better aromatic property and lower formation enthalpy than other allotropes.

We employ crystal orbital Hamilton population (COHP) to analyze the bond strength quantitatively. COHP is an energy-weighted DOS, which describes bonding and antibonding state arrangements in the band energy scale. Moreover, −1COHP was used to estimate the overlap strength of N–N bonds and Li–N bonds, which was calculated by using the LOBSTER program.52 The larger positive value means stronger bonding between two atoms. As shown in Figure S5, the −1COHP is 0.58–0.72 for Li–N bonds and 13.89–13.93 for N–N bonds in P6322-LiN5, which again revealed that there formed a strong chemical bond

![Figure 5. Sectional view of ELF along the cyclo-N5− plane of (a) P6322-LiN5, (b) P212121-LiN5, (c) P212121-LiN5, and (d) Pnan-LiN5 at 1 atm. The Bader charge of each atom is marked in the structures of (e) P6322-LiN5, (f) P212121-LiN5, (g) P212121-LiN5, and (h) Pnan-LiN5 at 1 atm. The integrated crystal orbital Hamilton populations (ICOHPs) between Li and N atoms and between N and N atoms are marked in the structures of (i) P6322-LiN5, (j) P212121-LiN5, (k) P212121-LiN5, and (l) Pnan-LiN5 at 1 atm.](https://dx.doi.org/10.1021/acsomega.0c03835)
between Li−N and N−N, and N−N bonds are much stronger than Li−N bonds, and the Li−N bonds would be broken first in AIMD simulations. For other LiN₅ allotropes (Figure 5h–l), the ICOHP is 0.69−0.85 for Li−N bonds and 13.84−14.45 of N−N bonds, and the bond strength of Li−N is a bit stronger than P6₂₂₂-LiN₅, but the homogeneity of N−N bond is a bit weaker than P6₂₂₂-LiN₅.

The calculated electronic band structure of LiN₅ allotropes is shown in Figure 6a–d. The results reveal that these two LiN₅ compounds are both semiconductors with a large band gap (both than 5 eV) at the PBE level at 1 atm. Considering density functional calculations usually lead to a considerable underestimation of the energy gap, and the actual band gaps are expected to be larger than the calculated results, thus the LiN₅ compounds would present the transparent crystal at ambient conditions because large optical band gap will induce weak visible light absorption. The band gap as a function of pressure is shown in Figure S5 from the range of 0−15 and 0−100 GPa. The band gap of all LiN₅ allotropes decreases with the increase of pressure, and they still show a big band gap at high pressure except P6₂₂₂-LiN₅, which is consistent with the experimental phenomenon that microphotographs appear translucent at 52.0 GPa.

The Raman spectrum of experimental data and all the LiN₅ allotropes under ambient conditions is shown in Figure 7, and more detailed low-intensity Raman peaks are shown in Figure S6. The calculated results reveal that the breathing and stretching cycle-N₅⁻ Raman modes could still be measured at peaks around 1200, 1130, and 1035 cm⁻¹ in all LiN₅ allotropes. The faint low-frequency peak (364 cm⁻¹) is observed in P₂₁₂₁₂₁-LiN₅, P₂₁/c-LiN₅, and P₆₁₂₂-LiN₅ (both 374 cm⁻¹), and these results are well consistent with the experimental. Moreover, many newly observed low-intensity peaks are marked in Figure 7, and except P₆₂₂₂-LiN₅ all other allotropes are possible to exist or coexist in experimental synthetic samples, which could be used to make clear that why Laniel et al. cannot get solely the diffraction lines of the LiN₅ compounds despite many attempts.

4. CONCLUSIONS

In summary, here, we reported three new LiN₅ compounds with negative formation enthalpy and supplemented the structure phases between 0 and 15 GPa. The stability of them is both confirmed by the phonon simulations, AIMD simulations, and bonding analysis. The calculated results reveal that the N−N bonds are harder to decompose than Li−N bonds, and the cycle-N₅⁻ can be maintained at least to 600 K, which is enough to be as
a metastable explosive material at ambient conditions. The electronic calculations suggest that these allotropes are transparent crystals. Also, the similar formation enthalpy, coordination features, electronic structure, and Raman spectrum indicate that these allotropes show great possibility of coexisting at atmospheric pressure, which could be used to explain that why Laniel et al. could not obtain solely the diffraction lines of the LiN₅ compounds despite many attempts. Moreover, our calculated results also reveal that LiN₅ could be applied under a strong oxidant environment (energy density is up to 3.78 kJ/g).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03835.

Crystal detail; formation enthalpies under 0–100 GPa; AIMD simulations results at 800 K; band gap change with pressure; Bader charge of known pentazolates; and Raman spectrum with low-intensity peaks (PDF)

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Notes
The authors declare no competing financial interest.

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