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The relevancy of the $[\text{B}_2\text{N}_4]$ substructure in the electronic structure of the metal-rich lanthanum nitridoborate $\text{La}_3(\text{B}_2\text{N}_4)$

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Abstract

Lanthanoid nitridoborates of the general formula $\text{Ln}_3(\text{B}_2\text{N}_4)$ with $\text{Ln} = \text{La}, \text{Ce}, \text{Pr},$ and Nd occur as black crystalline materials. Their structures contain oxalate-like $[\text{B}_2\text{N}_4]^{8-}$ ions being stacked in an eclipsed formation along one crystallographic direction. Electronic structures were calculated for a molecular $[\text{B}_2\text{N}_4]^{8-}$, for the $[\text{B}_2\text{N}_4]$ partial structure, and for the complete $\text{La}_3(\text{B}_2\text{N}_4)$ structure with the extended Hückel algorithm to analyze the bonding characteristics and to trace the necessity and properties of one surplus electron of $(\text{La}^{3+})_3(\text{B}_2\text{N}_4^{8-})(e^-)$. The HOMO of a $[\text{B}_2\text{N}_4]^{8-}$ is B–B σ bonding, and the LUMO is B–B π bonding but B–N antibonding. The energy band of the solid state $[\text{B}_2\text{N}_4]$ partial structure corresponding to the LUMO is broadened as a result of intermolecular B...B interactions between adjacent $[\text{B}_2\text{N}_4]$ units along the stacking direction. Due to bonding interactions with La d orbitals, this band is significantly lowered in energy and occupied with one electron in the band structure of $\text{La}_3(\text{B}_2\text{N}_4)$. This singly occupied band exhibits no band crossings but creates a semimetal-like band structure situation.

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Keywords: Electronic structure; Nitridoborate; Lanthanum

1. Introduction

Recently the chemistry of lanthanide nitridoborates reviewed as a new class of materials [1]. Several structures containing molecular anions such as $[\text{BN}]^{2-}$, $[\text{BN}_2]^{3-}$, $[\text{B}_2\text{N}_4]^{m-}$, $[\text{B}_3\text{N}_6]^{9-}$, and $[\text{BN}_3]^{6-}$ have been discovered and structurally characterized. Nitridoborate(nitride)s are known also for the alkaline earth compounds $E_3(\text{BN}_2)_2$ with $E = \text{Ca}, \text{Sr}, \text{Ba}$ [2] and $E_3(\text{BN}_2)\text{N}$ with Mg, Ca [3]. The electrical properties of all these compounds range from transparent insulators to black metals and superconductors. Black compounds have been obtained with $[\text{BN}]^{2-}$ and $[\text{B}_2\text{N}_4]^{m-}$ anions. So far, the only superconducting compound is $\text{La}_3\text{Ni}_2(\text{BN})_2\text{N}$ with the maximum superconducting transition temperature reported at $T_c = 14 \text{ K}$ [4]. Related compounds $\text{LnNi}(\text{BN})$ with $\text{Ln} = \text{Ca}, \text{La}, \text{Ce}, \text{Pr}$ have been identified and recently subjected to tight-binding band calculations for the case of $\text{Ln} = \text{Ca}$ and La [5,1].

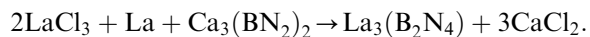
During the past years it has been shown that tight-binding band structure calculations can provide useful insights into properties and structural preferences of compounds in solid state [6]. In spite of the absence of superconductivity, the metal-rich family members $\text{Ln}_{3+x}(\text{B}_2\text{N}_4)\text{N}_x$ for $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ with $x = 0, 1, 2$ are considered as electronically unusual materials because there is no obvious reason why these compounds occur metal-rich when they are compared with salt-like compounds containing $[\text{BN}_2]^{3-}$, $[\text{BN}_3]^{6-}$, or $[\text{B}_3\text{N}_6]^{9-}$ ions [1]. The compounds $\text{Ln}_{3+x}(\text{B}_2\text{N}_4)\text{N}_x$ are known as air-sensitive black crystalline materials. $\text{La}_3(\text{B}_2\text{N}_4)$ [7] is considered as a good example for theoretical studies [8], not only because its structure is relatively simple, but also because it has no f -electrons and can be regarded as to contain trivalent lanthanum. The structure of $[\text{B}_2\text{N}_4]^{m-}$ merits the structure of the oxalate ion, $[\text{C}_2\text{O}_4]^{2-}$. Considering similar bonding conditions and the same number of electrons, the bis-dinitridoborate ion can be addressed as $[\text{B}_2\text{N}_4]^{8-}$.

It is interesting to note that a compound with the same sum formula as for $\text{La}_3(\text{B}_2\text{N}_4)$ is well-known for alkaline earth dinitridoborates. These dinitridoborates, such as $\text{Ca}_3(\text{BN}_2)_2$, contain linear $[\text{N} = \text{B} = \text{N}]^{3-}$ ions.

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We can easily imagine a reductive dimerization mechanism that could couple two dinitridoborate ions to yield one bis-dinitridoborate ion owing a B–B single bond, as obtained experimentally in reductive metathesis reactions [9]:



However no mixed phases were obtained through systematically doping experiments of Ca^{2+} into the $\text{La}_3(\text{B}_2\text{N}_4)$ structure or of La^{3+} into $\text{Ca}_3(\text{BN}_2)_2$, except for one unidentified phase. A corresponding reductive conversion of CO_2 molecules into $[\text{C}_2\text{O}_4]^{2-}$ has been reported as well [10]. Any further reduction from $\text{Ca}(\text{C}_2\text{O}_4)$ into a metal-rich oxalate such as “ $\text{La}(\text{C}_2\text{O}_4)$ ” is, however, unknown.

Colorless (or slightly yellow) $\text{Ca}_3(\text{BN}_2)_2$ is considered as an insulator, whereas black $\text{La}_3(\text{B}_2\text{N}_4)$ may be a semiconductor or a metal because it hosts one surplus electron. It will be interesting to trace this electron and to find out if it is located at the metal as $(\text{La}_3 \cdot e^-)(\text{B}_2\text{N}_4)$ or at the nitridoborate as $\text{La}_3(\text{B}_2\text{N}_4 \cdot e^-)$ and for what reason this metal-rich compound is favored more than a salt-like, e.g., the La deficient composition $\text{La}_{3-x}(\text{B}_2\text{N}_4)$ with $x = \frac{1}{3}$.

2. Description of the crystal structure

$\text{La}_3(\text{B}_2\text{N}_4)$ belongs to the family of lanthanoid nitridoborate(nitride)s $\text{Ln}_{3+x}(\text{B}_2\text{N}_4)\text{N}_x$ with $x = 0, 1, 2$. These compounds exhibit a very unique structural pattern in which nitride ions reside in octahedral (distorted) formations of Ln atoms. Boron atoms of bis-dinitridoborate are surrounded in nearly trigonal-prismatic formations of La atoms, such that trigonal prisms of adjacent boron atoms share one rectangular

face to yield a double prism (Fig. 1). In all structures these $[\text{La}_8(\text{B}_2\text{N}_4)]$ units share rhombic faces to form $[\text{La}_{8/2}(\text{B}_2\text{N}_4)]$ columns with the a -axis repeat of 362.94(3) pm. Nitrogen atoms of the bis-dinitridoborate are capped by a square pyramidal formation of Ln atoms. These local environments can be used to construct all structural members of the $\text{Ln}_{3+x}(\text{B}_2\text{N}_4)\text{N}_x$ family.

Following this structural pattern $\text{La}_3(\text{B}_2\text{N}_4)$ crystallizes orthorhombic, $Immm$, $a = 362.94(3)$ pm, $b = 641.25(6)$ pm, $c = 1097.20(8)$ pm with two formula units per unit cell [7]. In our calculation of the electronic structure the body centered unit cell was reduced to obtain a primitive cell with one formula unit and the new set of basis vectors $a' = b' = c' = 660.8$ pm, $\alpha = 148.12^\circ$, $\beta = 67.77^\circ$, and $\gamma = 121.95^\circ$ as derived from the old set of lattice constants by the transformation: $a' = \frac{1}{2}(a, b, -c)$; $b' = \frac{1}{2}(-a, b, c)$; $c' = \frac{1}{2}(a, -b, c)$.

3. Molecular orbitals of the $[\text{B}_2\text{N}_4]$ anion and the band structure of $[\text{B}_2\text{N}_4]$ in solid state

At first we calculate the MO of the planar $[\text{B}_2\text{N}_4]^{8-}$ unit (D_{2h} point symmetry) with B–B distances of 182 pm, B–N distances of 150 pm, and N–B–N and B–B–N angles of $120 \pm 1^\circ$, as adopted from the crystal structure. In the MO scheme shown in Fig. 2 we note four low-lying B–N σ bonds and twelve nitrogen centered MO's clearly higher in energy, of which some exhibit some weaker B–N π bonding interactions. The HOMO contains a strong B–B σ bond and is separated by an energy gap in the order of 4 eV below the LUMO. The bonding B–B and the weakly antibonding B–N energy level corresponding to the LUMO of $[\text{B}_2\text{N}_4]^{8-}$ remains unoccupied. For a LUMO with these

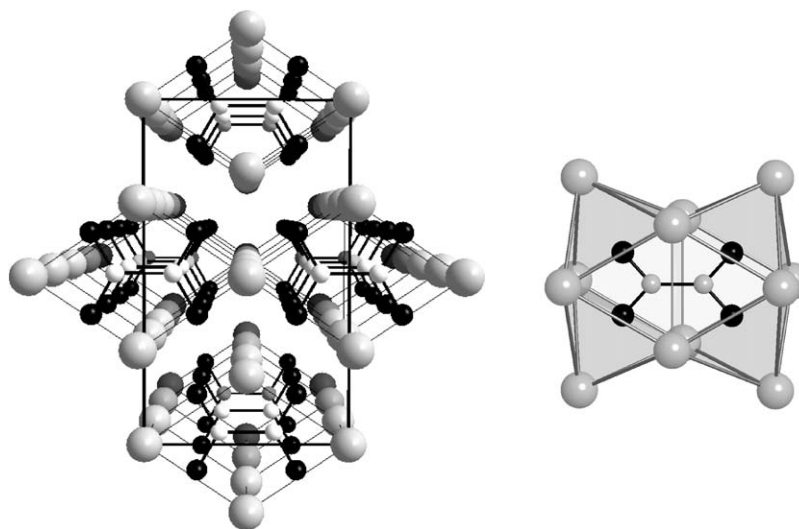


Fig. 1. Perspective projection of the structure of $\text{La}_3(\text{B}_2\text{N}_4)$ along [100] (left) and environment of $[\text{B}_2\text{N}_4]$ with La atoms (right). La is shown light gray, B in white, and N in black.

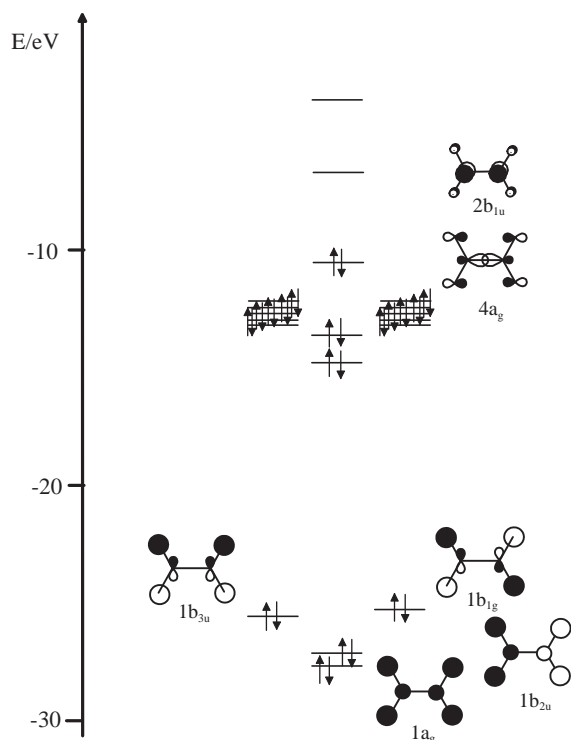
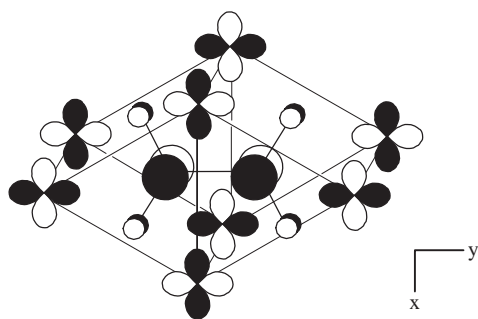


Fig. 2. MO scheme of $[\text{B}_2\text{N}_4]^{8-}$ with some relevant orbital combinations drawn.

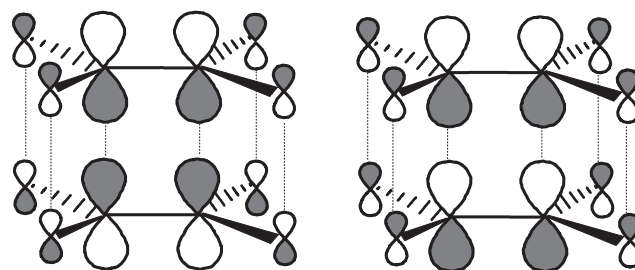
characteristics we could imagine an occupation with two electrons leading to the hypothetical $[\text{B}_2\text{N}_4]^{10-}$ ion with a B–B double bond and four B–N σ bonds. Once the $[\text{B}_2\text{N}_4]$ unit is surrounded with lanthanum atoms in a double trigonal prismatic environment, the LUMO is lowered in energy by about 2 eV through bonding interactions through La orbital mixing. In a localized MO picture this bonding interaction can be illustrated through interactions with $d_{x^2-y^2}$ orbitals of La as shown for a $[\text{La}_8(\text{B}_2\text{N}_4)]$ unit in Scheme 1.



Scheme 1.

The band structure of the $[\text{B}_2\text{N}_4]$ substructure is projected in Fig. 3, together with the projected density of states (DOS), and the crystal orbital overlap populations (COOP) showing the (intramolecular) B–B and B–N interactions. The strongly B–B σ bonding characteristic (near -11 eV) in the COOP can be well

compared with the corresponding HOMO combination illustrated in Fig. 2. The energy band corresponding to the LUMO exhibits a pronounced band broadening (around -8 eV) along the reciprocal space direction between the special points X and T [11], corresponding to the stacking direction of the $[\text{B}_2\text{N}_4]$ units parallel [100] in real space. An inspection of this broadening reveals that orbital interactions between boron atoms of adjacent $[\text{B}_2\text{N}_4]$ units are of special importance. The bonding and antibonding B...B σ interactions (at the T and X points) between boron atoms of adjacent $[\text{B}_2\text{N}_4]$ units are illustrated for two $[\text{B}_2\text{N}_4]$ units in a localized presentation in Scheme 2.



Scheme 2.

The energy band centered around -8 eV remains unimportant in the $[\text{B}_2\text{N}_4]^{8-}$ substructure because it is unoccupied. With one surplus electron the bonding portion of this band will be occupied and the antibonding portion will be empty. Therefore, conditions for a stable $[\text{B}_2\text{N}_4(\text{e}^-)]^{9-}$ anionic substructure are electronically fulfilled through intermolecular B–B σ bonding.

4. Band structure of $\text{La}_3(\text{B}_2\text{N}_4)$

The band structure of $\text{La}_3(\text{B}_2\text{N}_4)$, projected in Fig. 4, can be easily derived from the band structure of the $[\text{B}_2\text{N}_4]$ substructure in Fig. 3. The energy band corresponding with the HOMO of $[\text{B}_2\text{N}_4]^{8-}$ remains nearly unchanged, being localized slightly above -12 eV. The curve-nature of the band corresponding with the LUMO is slightly altered through mixing with orbitals of lanthanum. Still, the same band dispersion pattern resulting from intermolecular B–B bonding is obtained between the X and T points. This band contains dominant lanthanum orbital contributions as shown by the projected DOS and is half-occupied as indicated by the position of the Fermi level (dotted line) in Fig. 4.

5. Results and discussion

The electronic structure of $\text{La}_3(\text{B}_2\text{N}_4)$ is characterized by anionic interactions constructed from boron–boron interactions due to eclipsed stacking of $[\text{B}_2\text{N}_4]$ units in

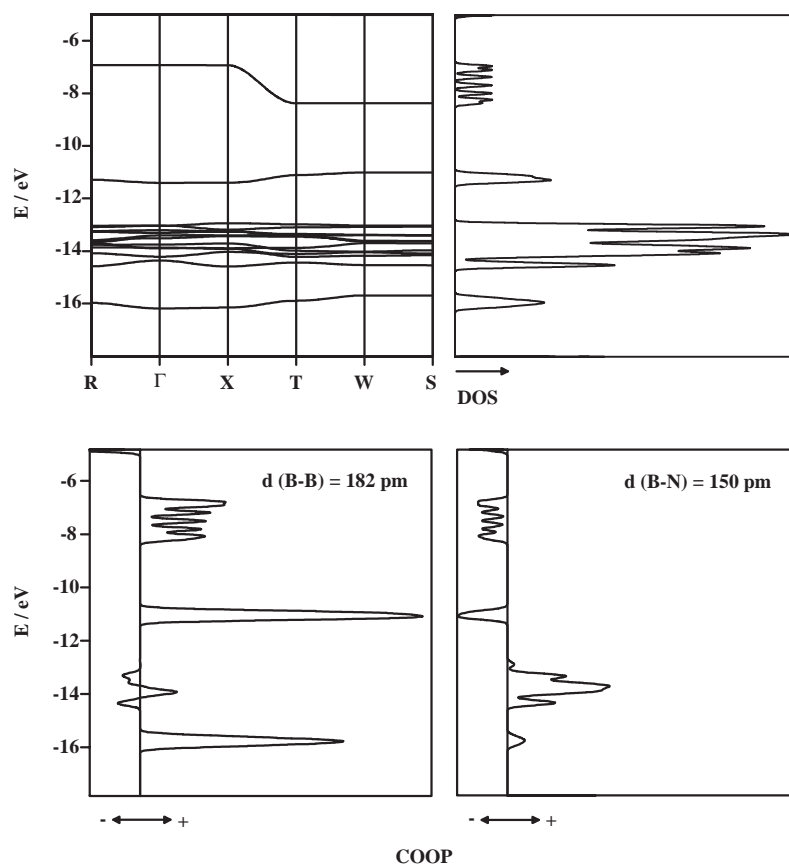


Fig. 3. Band structure and DOS of the [B₂N₄] partial structure (top) and COOP for intramolecular B–B and B–N interactions (bottom).

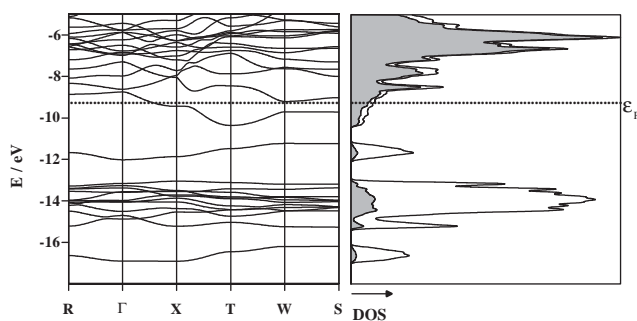


Fig. 4. Band structure and DOS of La₃(B₂N₄). Contributions of metal states to the total DOS are shown gray. The Fermi level (ε_F) is indicated as a dotted line.

the structure. The interaction can be well understood when electronic states of the isolated [B₂N₄]⁸⁻ ion are compared with those of the [B₂N₄] stacking structure.

The HOMO of molecular [B₂N₄]⁸⁻ is strongly B–B σ bonding and the LUMO has B–B π bonding but B–N antibonding character. If arranged in the one-dimensional polymeric [B₂N₄]⁸⁻ structure, the LUMO's of the [B₂N₄]⁸⁻ units can interact through intermolecular B–B σ bonding of adjacent [B₂N₄] units to form a band. The band width of the [B₂N₄] structure is a measure for the intermolecular B–B orbital interaction along the stack-

ing direction (between special points X and T in reciprocal space), that strongly depends on the dimension of the lattice parameter *a*, as in a simple band structure of an infinite σ bonded chain of *p* orbitals. An electronic equilibrium is obtained with a half-filled band situation, were all (intermolecular) bonding B–B σ states are occupied, corresponding with [B₂N₄(e⁻)]⁹⁻, and all antibonding B–B σ states empty.

In the band structure of La₃(B₂N₄) the intermolecular B···B σ bonding is located at the bottom of the metal states dominated *d* block. The band dispersion of the highest occupied energy band is not only due to intermolecular B···B σ interactions but also contains significant orbital mixing with lanthanum orbitals. The presence of one surplus electron of (La³⁺)₃(B₂N₄⁸⁻)(e⁻) favors the present eclipsed stacking pattern of [B₂N₄] units in the structure through occupation of all intermolecular B···B σ bonding states, similar as for the partial [B₂N₄] structure. In contrast, all salt-like nitridoborates adopt structures with B···N stacking alternations similar as in the hexagonal BN structure. The band width of the half-occupied conduction band of less than 2 eV in La₃(B₂N₄) is relatively small to make a good conductor. An indirect band gap in the band structure gives raise to expect semimetal behavior of La₃(B₂N₄), consistent with the black color of the

material and temperature independent paramagnetism. The occurrence of Ce^{4+} in the homologous cerium compound [7] may be less favored because antibonding $\text{B}\cdots\text{B}$ σ interactions between adjacent $[\text{B}_2\text{N}_4]$ units will destabilize the mixed valence compound $(\text{Ce}^{4+})(\text{Ce}^{3+})_2(\text{B}_2\text{N}_4^{8-})(\text{e}^-)_2$ through an (not observed) increase along the stacking direction.

The partial occupation of the B–B bonding π level (LUMO) and the intermolecular orbital mixing with other π levels through $\text{B}\cdots\text{B}$ σ bonding and orbital mixing with La orbitals determines the conductivity behavior of $\text{La}_3(\text{B}_2\text{N}_4)$. A critical role of anionic π levels on the electronic properties of materials has been obtained for metal dicarbides with $[\text{C}_2]^{n-}$ units, where the C–C distance increases with the occupation of C–C antibonding π_g levels, along the row of dicarbides CaC_2 , LaC_2 , UC_2 . However, no characteristic shortening is obtained for the B–B bond distance in $[\text{B}_2\text{N}_4]$ of $\text{La}_3(\text{B}_2\text{N}_4)$ through partial occupation of states having intramolecular B–B π bonding and intermolecular B–B σ bonding nature in a rectangular arrangement of four boron atoms. The obtained B–B bond distances in the series of $\text{Ln}_3(\text{B}_2\text{N}_4)$ compounds with $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ show no significant deviations (180 ± 3 pm). The corresponding B–B distance in the non-planar $\text{B}_2\text{N}_4(\text{CH}_3)_8$ was reported at 176.2 pm [12].

Similar electronic conditions and orbital mixtures as for $[\text{B}_2\text{N}_4]$ are obtained from MO calculations performed for the $[\text{C}_2\text{O}_4]^{2-}$ ion (with the LUMO at -10 eV and a HOMO–LUMO gap in the order of 3 eV). Therefore, chances may exist to synthesize metal-rich oxalates with electropositive metals under appropriate conditions.

Acknowledgments

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Appendix A

Tight-binding extended Hückel calculations [13,14], with a weighted H_{ij} approximation, have been applied

throughout this paper.¹ Band structure calculations were performed using a set of 100 k points along each special direction of the Brillouin zone [11].

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¹The extended Hückel parameters used throughout all calculations of the electronic structure are: La 5d: $H_{ii} = -8.21$ eV, $\zeta_1 = 3.78$, $\zeta_2 = 1.381$, $c_1 = 0.7765$, $c_2 = 0.4586$; La 6s: $H_{ii} = -7.67$ eV, $\zeta = 2.14$; La 6p: $H_{ii} = -5.01$ eV, $\zeta = 2.08$; B 2s: $H_{ii} = -15.2$ eV, $\zeta = 1.3$; B 2p: $H_{ii} = -8.5$ eV, $\zeta = 1.3$; N 2s: $H_{ii} = -26.0$ eV, $\zeta = 1.95$; N 2p: $H_{ii} = -13.4$ eV, $\zeta = 1.95$.