Theoretical Study on the Stability of the Noble-Gas Containing Anions：HBNNgBN$^-$ (Ng ≡ He, Ne, Ar, Kr and Xe)

Ying-Jhun He and Wei-Ping Hu *

Department of Chemistry and Biochemistry, National Chung Cheng University, Chiayi, Taiwan

Abstract

The current computational study searches for stable noble-gas containing anions that do not include fluorine or oxygen atoms. The designed molecules are HBN$^-$…NgBN (Ng = He, Ne, Ar, Kr and Xe). The stability mainly comes from the inductive effect of HBN$^-$, which strengthens the chemical bonding of Ng−B. For Ng = Ar, Kr and Xe ,the three-body and two-body dissociation energies were found to be higher than 36.1 kcal/mol and 13.7 kcal/mol, respectively. These new type of anions are expected to be stable at low temperature.

Introduction

The noble gas elements discovered in the 1890s have long been considered chemically inert. The reactivity of noble gases is rather poor because the valence shells of noble gases are completely filled. It is very difficult to give an electron to a noble gas atom or to take an electron from it. In 1933, Linus Pauling published a paper predicting the existence of H_4XeO_6, XeF_6, and KrF_6. In 1962, Bartlett synthesized $Xe[PtF]_6$, the first stable noble gas compound. Since then, many stable and halogen-containing noble gas have been discovered experimentally or predicted by theoretical calculations. Most of the stable noble gas-containing molecules or anions contains fluorine or oxygen. A stable noble gas anion FNgO$^-$ has been predicted in our laboratories, and this opened the field of anionic noble gas chemistry. In this study, the fluorine and oxygen atoms were replaced by the HBN and BN groups, forming a new series of fluorine-less and oxygen-less stable noble-gas containing anions.

Methods

MP2 and CCSD(T) electronic structure theory are used, and the basis sets used are the Dunning-type aug-cc-pVDZ and aug-cc-pVTZ. They are abbreviated as apdz and aptz hereafter. For Ar the basis set of aug-cc-pV(D+d)Z and aug-cc-pV(T+d)Z basis sets are used. For Xe, the aug-cc-pVDZ-pp and aug-cc-pVTZ-pp basis sets are used in which a relativistic pseudo-potential is used for core electrons. Electronic structure and charge distribution calculations were performed using Gaussian 16. The following structures are obtained at MP2/apdz level, and energies at CCSD(T)/aptz level.

Results and Discussion

The Ng-N and Ng-B bond length of HBNNgBN$^-$ increases with the increase of noble gas atomic number. For Ng = Ne-Xe, HBN…Ng distances are almost the same.
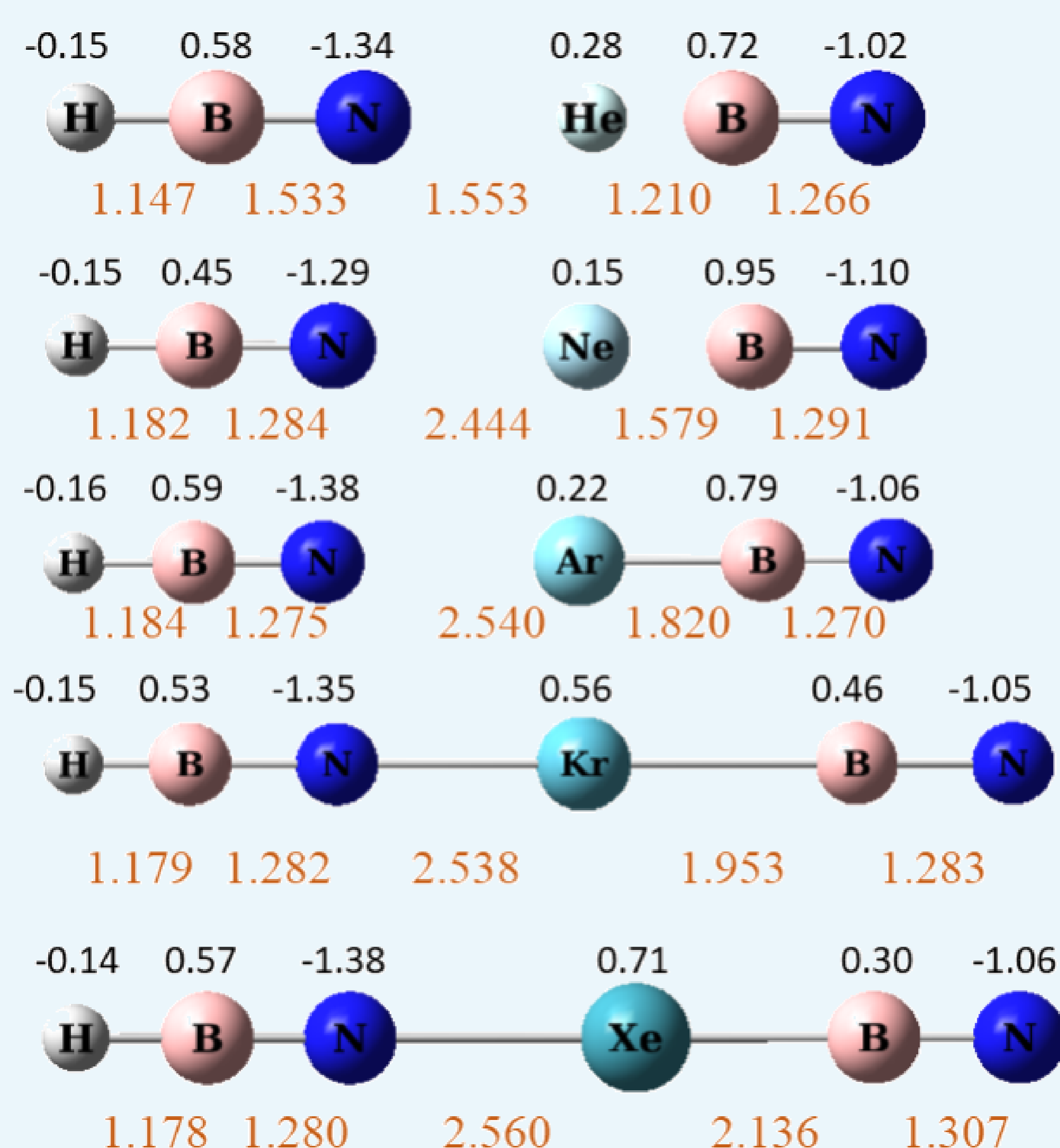
Figure1. Structure of HBNNgBN$^-$ (Ng = He, Ne, Ar, Kr and Xe). The orange values are the bond lengths , unit：Å. Black values are NBO atomic charges.

Table 1. Dissociation energies and barrier heights of HBNNgBN$^-$, unit: kcal/mol.

Ng	HBN$^-$ + Ng + BN	Barrier	HBNBN$^-$ + Ng
He	21.7	-2.2	-126.3
Ne	8.8	0.5	-139.2
Ar	37.7	13.7	-110.4
Kr	47.8	16.9	-100.3
Xe	62.4	23.7	-85.7
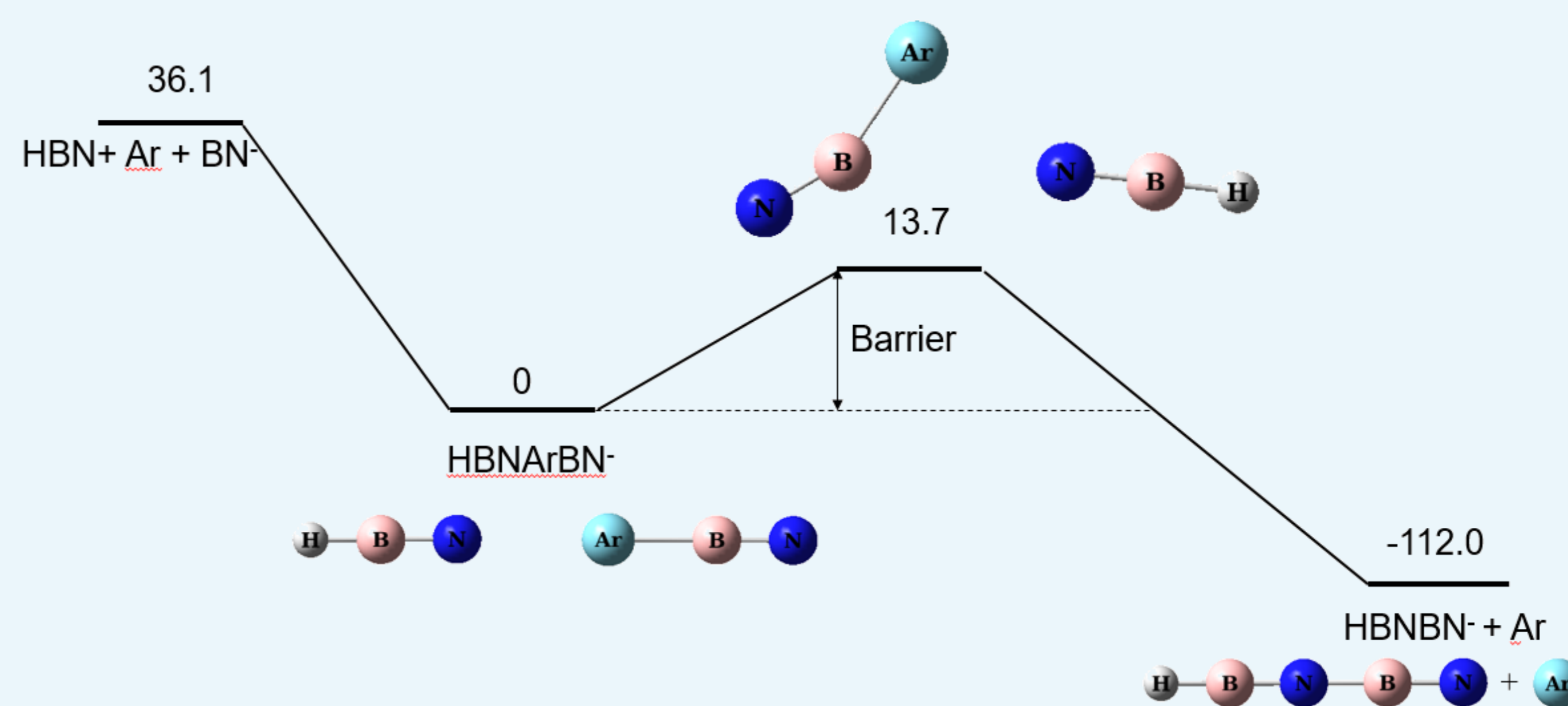
Figure2. The dissociation pathway of HBNArBN$^-$.

The electron density around Ng-BN is deformed, and the electron distribution is consistent to a covalent bond. On the other hand, HBN…Ng is more ionic in character.

The Laplacian of the electron density maps also hint that the HBN…Ng bonding are ionic and the rest are covalent.
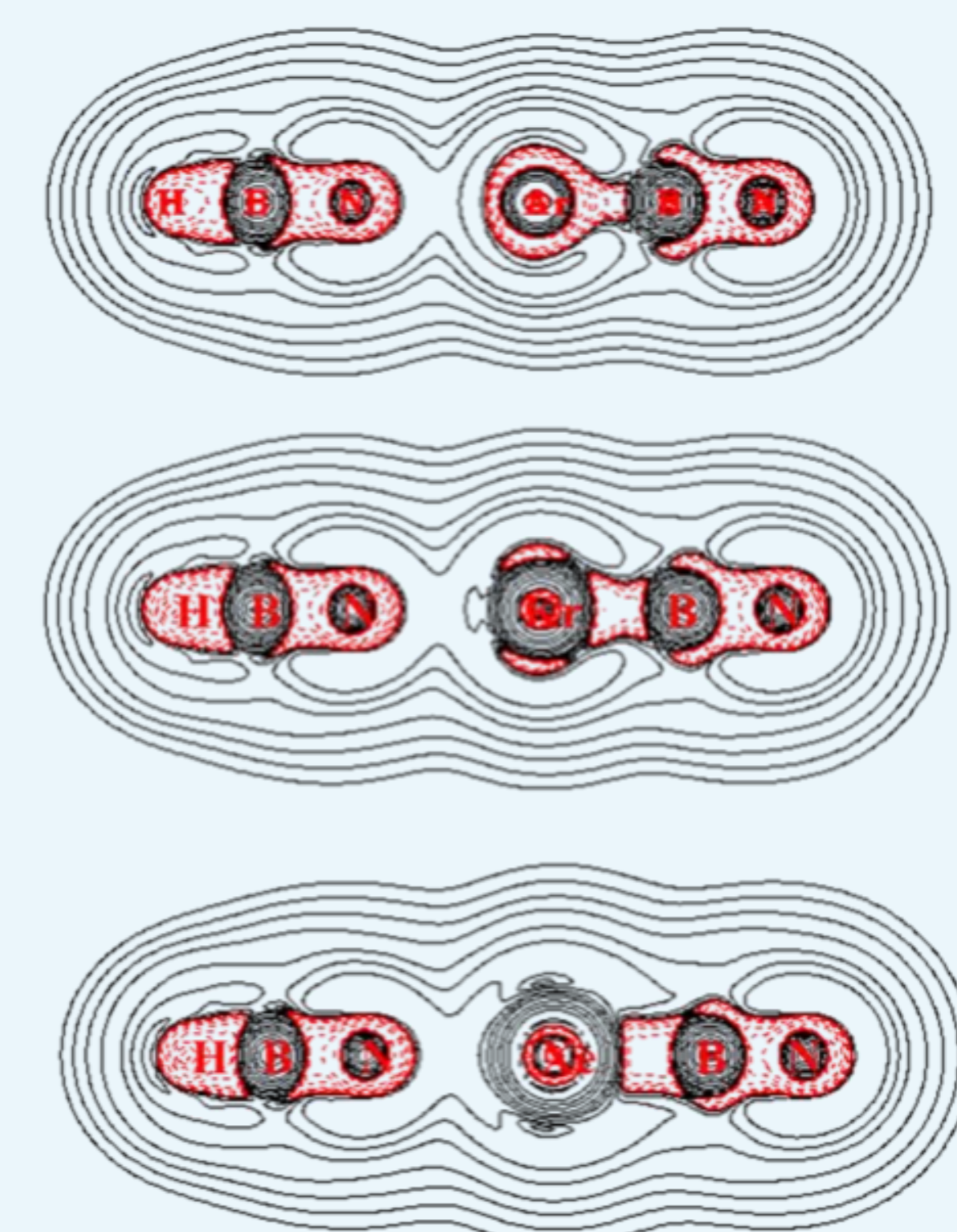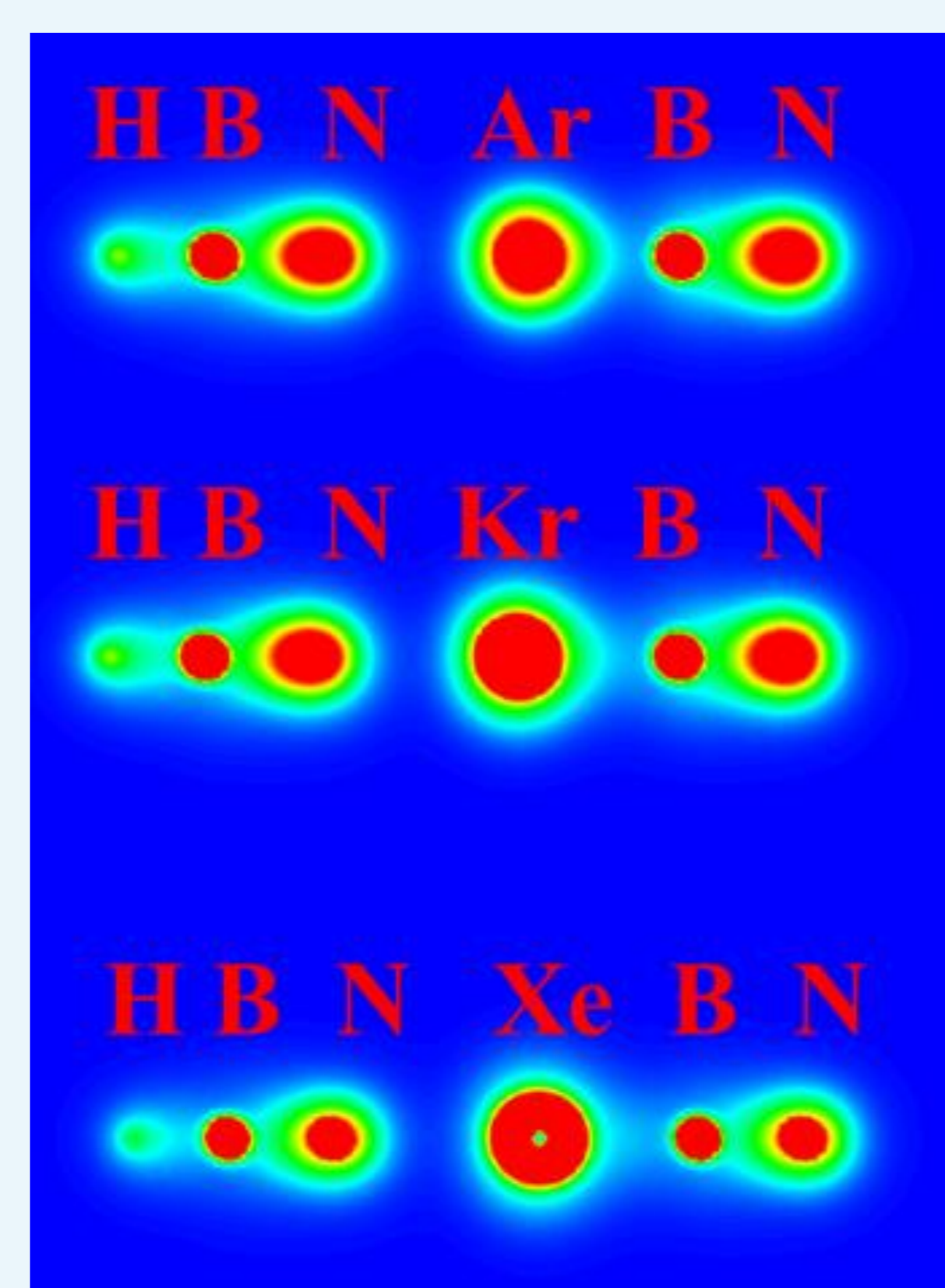
Figure 3. The electron density diagram of HBNArBN$^-$

Figure 4. HBNArBN$^-$ Laplaction concentration.

Conclusions

This study investigates the structures and stability of HBNNgBN$^-$. We found that all the anions are linear, and when the noble gas atoms are Ar, Kr and Xe, the anions are stable at low temperature. Importantly, the anions do not include any fluorine and oxygen atoms. The stability increases as the atomic number of the noble gas increases. We predict that these anions may be observed experimentally at low temperature. It can be seen from the NBO atomic charges (Figure 1) that Ng is positively charged and N is very negatively charged. As the atomic number of Ng increases, the value of positive charge on Ng increases. According to Figures 3 and 4, the region between HBN and Ng contains very lower electron density. This suggests that their bonding is ionic. The Ng−BN bonding is more covalent-like .

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