Stable molecules with noble-gas bonding to bicyclic aromatic substituents

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Abstract

We have designed a new type of noble gas (Ng) molecule featuring a bicyclic moiety, where two aromatic rings are connected by a C–C bond. The five-membered ring is either pyrrole or 1,2,3-triazole, while the six-membered ring is pyrimidine. Our motivation for expanding from one aromatic ring to two comes from our recent discovery: if the rings are connected in the appropriate positions and both contain nitrogen atoms, the stability of the noble gas molecule can be significantly enhanced. Preliminary studies indicate that for Ng = Ar, the stability against three-body unimolecular dissociation can be increased by about 15 kcal/mol with the addition of an extra ring.

Motivation

Although noble gases were initially regarded as almost nonreactive due to their completely filled valence shells, recent studies have shown that under special conditions they can form stable organic molecules.[1] In 2017, Khriachtche et al. reported the first aromatic and halogen-free cyclic noble gas compound, C_6H_5CCXeH, with matrix isolation.[2] Our laboratory has long been dedicated to the study of noble gas chemistry and the design of stable noble-gas molecules containing aromatic groups. In recent years, inspired by the click chemistry[3], we have designed the molecule FNg-1,2,3-triazole which showed high stability for Ng = Kr and Xe at low temperature.[4] Recently, we discovered that if one of the hydrogen on the triazole ring is replaced by a pyrimidine, the resulting molecules FNg-1,2,3-triazole-pyrimidine may possess significantly higher stability. Thus, the current research reports our computational study on the molecules and the related molecules FNg-pyrrole-pyrimidine for Ng = Ar, Kr, and Xe.

Methods

For geometry optimization and vibrational frequencies, we used Møller–Plesset second-order perturbation theory (MP2) with the aug-cc-pVDZ basis sets developed by Dunning et al. For the third-period element Ar, we use the aug-cc-pV(D+*d*)Z basis set with an additional set of *d* polarization functions. For Xe atom we employed the aug-cc-pVDZ-PP basis set which contains a relativistic core potential. For accurate relative energies, the coupled clusters theory CCSD(T) and the aug-cc-pVTZ and aug-cc-pVTZ-PP basis sets were used.

Result & discussion

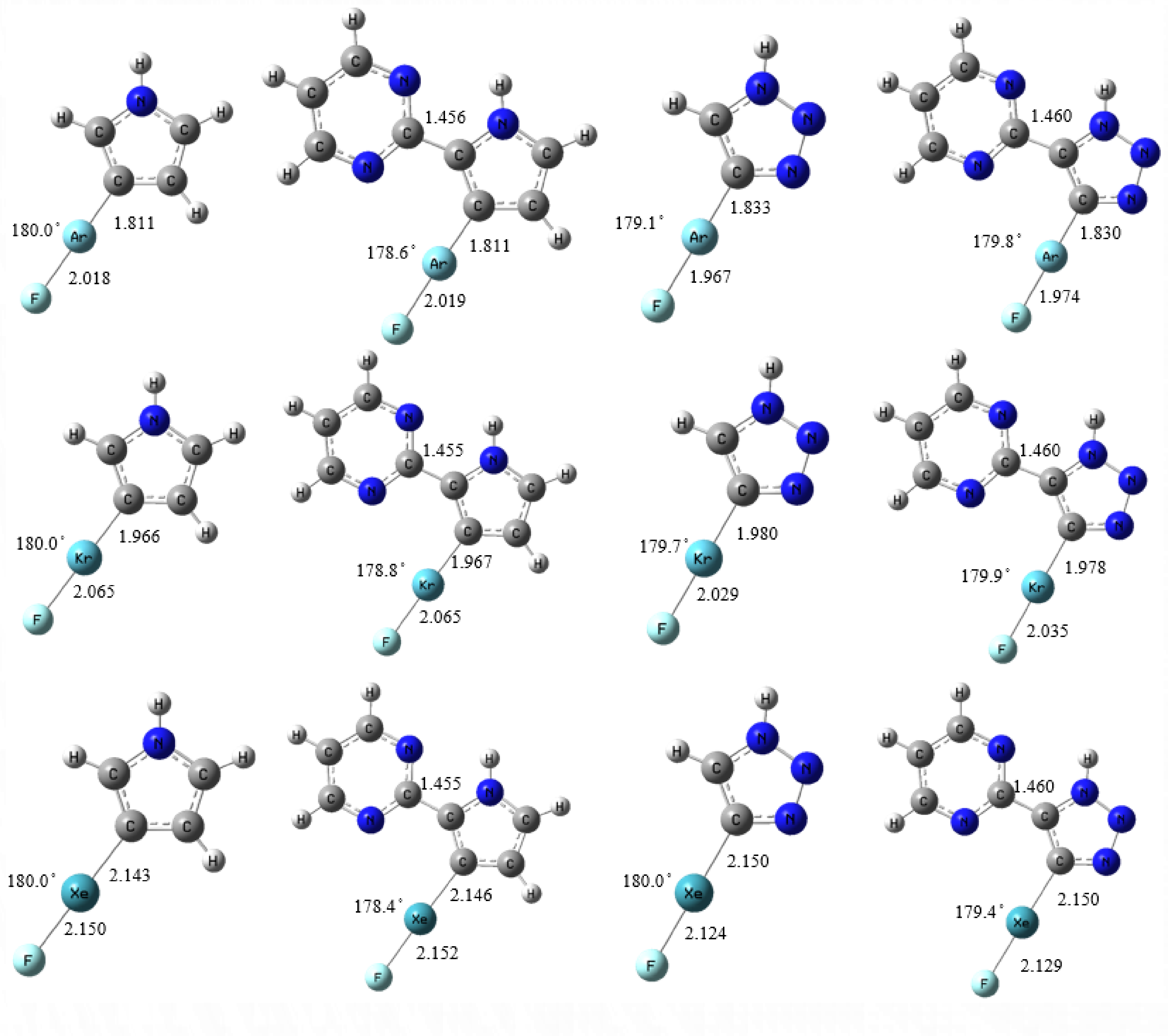

Figure 1. The calculated structures of FNg-pyrrole, FNg-pyrrole-pyrimidine, FNg-1,2,3-triazole and FNg-1,2,3-triazole-pyrimidine.

I. Structures

The calculated structures for Ng = Ar, Kr, Xe are shown in Figure 1. As the atomic number of the noble gas increases, the Ng–C bond length increases from approximately 1.80 Å to around 2.15 Å, and the Ng-F bond length also shows a slight increase. However, the C–C bonds connecting the two rings remain unchanged.

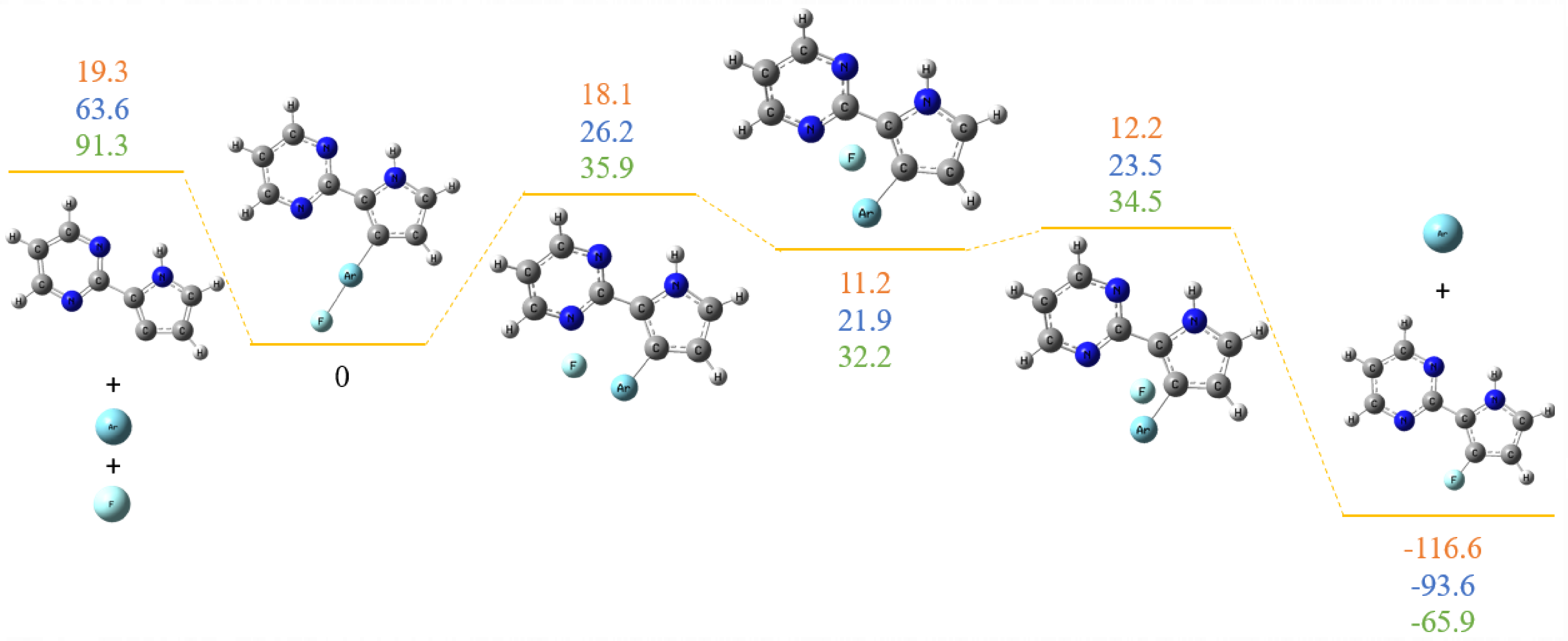

Figure 2. The calculated potential energy profile for the unimolecular dissociation pathways of FNg-pyrrole-pyrimidine. The orange, blue and green colors represent for Ng = Ar, Kr, and Xe, respectively. The energies for Kr and Xe were estimated using MP2/aug-cc-pVDZ.

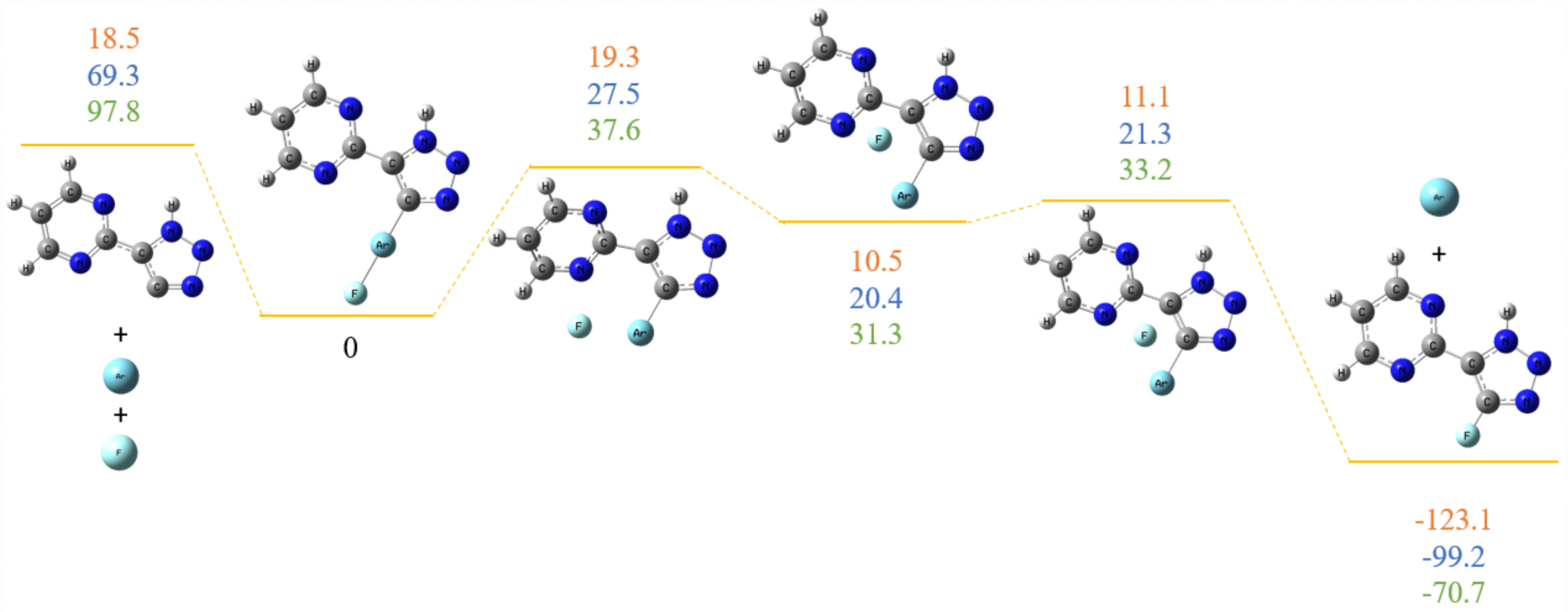

Figure 3. The calculated potential energy profile for the unimolecular dissociation pathways of FNg-1,2,3-triazole-pyrimidine. The orange, blue and green colors represent for Ng = Ar, Kr, and Xe, respectively. The energies for Kr and Xe were estimated using MP2/aug-cc-pVDZ.

II. Stability

As shown in Figures 2 and 3, both FNg-pyrrole-pyrimidine and FNg-1,2,3-triazole-pyrimidine exhibit very high stability, which suggests that these two molecules are likely to exist under low-temperature conditions. Notably, their linear dissociation energies are 20-25 kcal/mol higher than those of FNg-pyrrole and FNg-1,2,3-triazole, which lack pyrimidine substituent. For Ng = Ar, their three-body dissociation energies are 15 kcal/mol higher than that of HArF[5], the only observed Ar containing neutral molecule, at the same level of theory.

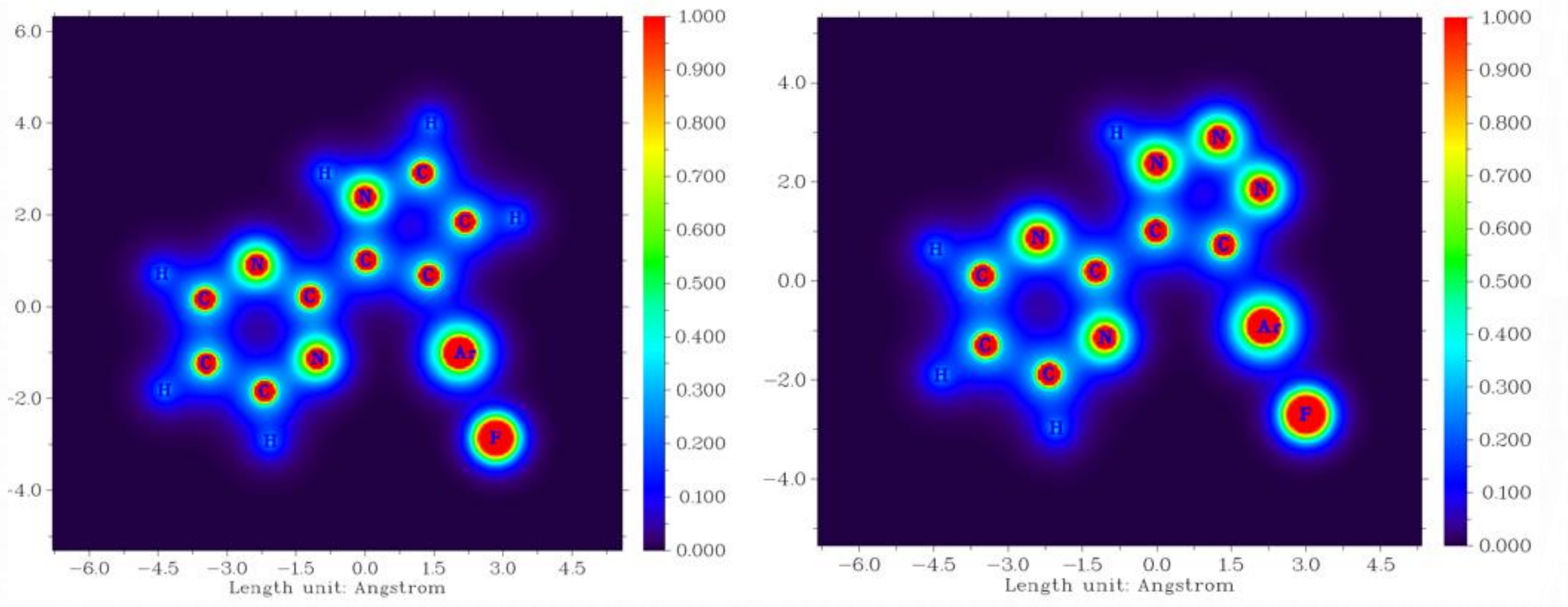

Figure 3. The electron density distribution of FNg-pyrrole-pyrimidine and FNg-1,2,3-triazole-pyrimidine . The color scale represents electron density, where red regions indicate higher electron density, and blue regions indicate lower electron density.

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The bond between F–Ng exhibits very low electron density, making it more similar to an ionic bond, whereas the Ng–C bond has a higher electron density, making it more similar to a covalent bond.

Conclusion

This study designs novel noble gas (Ng) molecules by expanding from a single to a dicyclic aromatic group, where nitrogen atoms are strategically positioned to enhance stability. Calculations showed that the three-body dissociation energies of FNg-pyrrole-pyrimidine and FNg-1,2,3-triazole-pyrimidine are 20-25 kcal/mol higher than those of FNg-pyrrole[6] and FNg-1,2,3-triazolel. This suggests that suitable aromatic substituents can significantly enhance the thermal stability of these noble gas molecules. We expect that the varieties of these noble gas molecules could be further expanded by connecting the ring to other functional groups and retain similar stability.

References

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