Theoretical Study of the Noble-Gas Containing Radical Anions XNgBCH$^-$ (X= O, S)

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Abstract

In this research, we study the noble-gas containing radical anions XNgBCH$^-$ (X=O, S and Ng= He–Xe) with theoretical calculations. The radicals were predicted to be linear in structure. When the noble gas is Ar, Kr and Xe, the anions were predicted to be stable against unimolecular dissociation. They might be experimentally observable at low temperature.

Motivations

Most of the noble-gas containing molecules found in theory or experiment are closed-shell molecules. The open-shell noble-gas containing radical molecules, such as HXeO [1] and HXeCC [2], are relatively rare. Stable polyatomic radical containing lighter noble gas such as argon have never been observed.

Most light noble-gas containing molecules contain fluorine atoms, and the bonding of noble gases to sulfur atoms is rarely stable. In the current study, we designed a new series of free radical molecules ONgBCH$^-$ and SNgBCH$^-$ which are fluorine-less and are expected to be stable.

Methods

Structure and Frequency. The electronic structure and frequency calculations were performed using MP2 and CCSD(T) theory with dunning-type basis sets aug-cc-pVnZ (n= D, T).

Energy. We use CCSD(T)/aug-cc-pVnZ (n= Q, 5) extrapolation to obtain complete basis set (CBS) [3] energies for estimating more accurate relative energies.

Software. The electronic structure and charge distribution calculations were performed using the *Gaussian 16*. Electron density maps were made using Multiwfn [4].

Results and Discussion

I. Structure and Charge Distribution. The structure of XNgBCH$^-$ (Ng= Ar, Kr, Xe) is linear. Figure 1 shows that the Ng–B bond length of XNgBCH$^-$ increases significantly (about 0.32 Å) with the increase of the noble-gas atomic number. We compare with the isoelectronic radical FNgBCH [5] and find that O–Ng is 0.4 Å longer than F–Ng, and Ng–B is also about 0.2 Å longer.

Figure 1 also shows the NPA atomic charges of XNgBCH$^-$. It shows that the negative charge is mainly concentrated on oxygen/sulfur and carbon atoms. As the Ng radius increases, the charge on the boron atom increases.

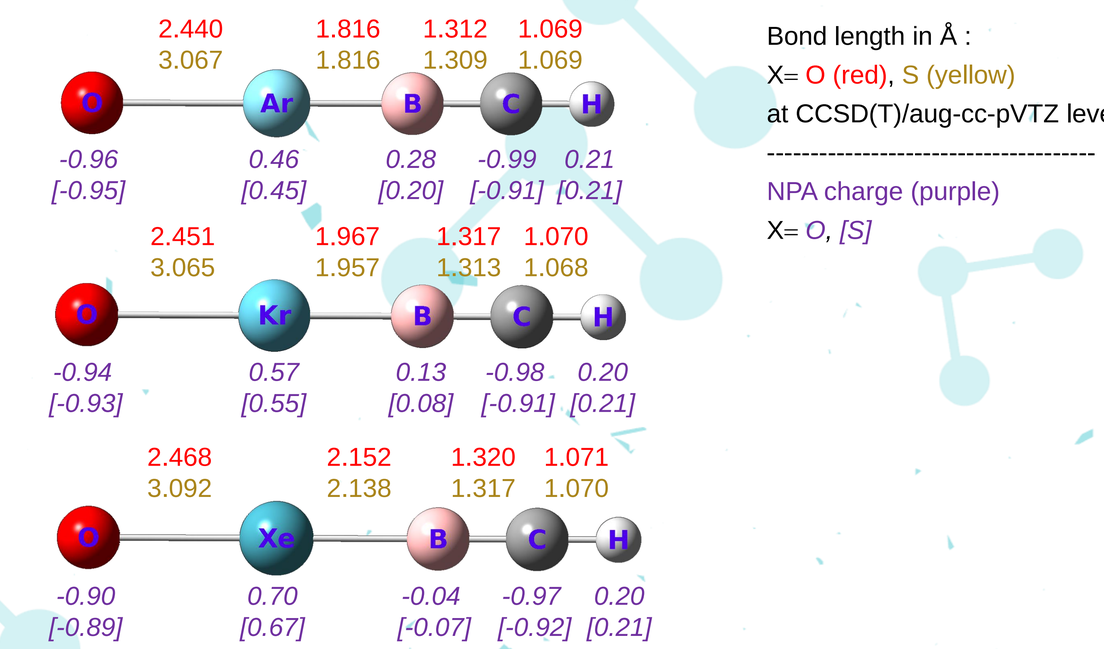

Figure 1. Calculated structures and NPA charges of XNgBCH$^-$.

II. Stability. Figure 2 and Table 1 show that both linear dissociation energy and barrier height of XNgBCH$^-$ (Ng= Ar–Xe) are higher than 13 kcal mol^{-1}. The linear dissociation energies of the FNgBCH (Ng= Ar–Xe) are 12.6, 31.6, 58.6 kcal mol^{-1}, and the barrier heights are 12.1, 19.3, 26.5 kcal mol^{-1}, respectively. It indicates that the stability of XNgBCH$^-$ is similar to that of FNgBCH.

III. Electron Density Maps. Figure 3 (a) shows that the electron density of Ng are polarized by the BCH functional group, which indicates that Ng–B is a covalent bond. Based on past experience, the charges of two atoms bonded by ionic bonds are usually very different (>1.2). The X–Ng is an ionic bond, which can be seen from Figures 1 and 3 (a).

Figure 3 (b) shows the spin density, which can tell us that the unpaired electron is mainly located on X and BCH. This means that the stability of the Ng bond is not easily to be destroyed.

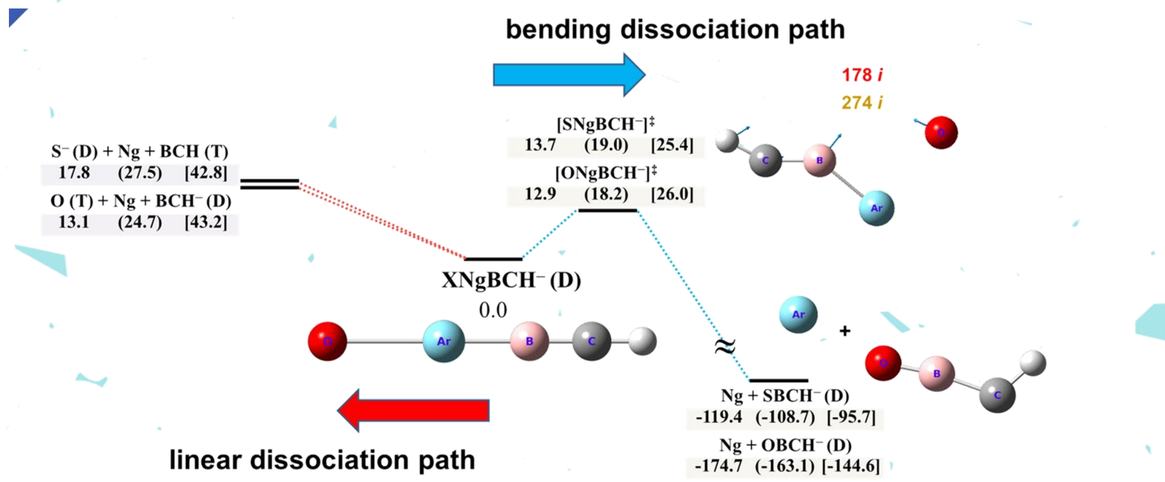

Figure 2. XNgBCH$^-$ dissociation pathway. The energy in kcal mol^{-1} and frequency in cm^{-1}. Ng= Ar (Kr) [Xe]

Table 1. **Linear dissociation energies of ONgBCH$^-$ in kcal mol^{-1}.**

Dissociation path	X–Ng					
	O–Ar	S–Ar	O–Kr	S–Kr	O–Xe	S–Xe
→ X (S) + Ng + BCH$^-$ (D)	63.0	48.0	74.5	57.7	93.0	73.0
→ X$^-$ (D) + Ng + BCH (S)	32.7	23.2	44.2	32.9	62.7	27.5
→ X$^-$ (D) + Ng + BCH (T)	27.3	17.8	38.8	27.5	57.3	42.8
→ X (T) + Ng + BCH$^-$ (D)	13.1	18.3	24.7	28.0	43.2	43.3

*All energies are relative to the XNgBCH$^-$ in the doublet state.

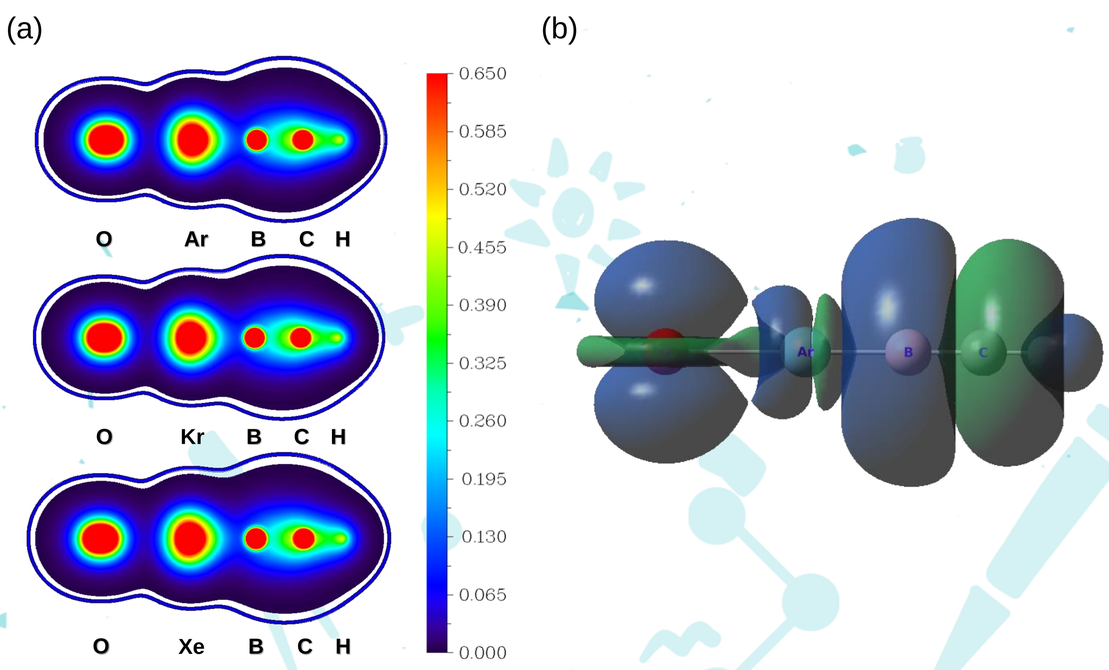

Figure 3. Electron density maps of ONgBCH$^-$. (a) From MP2 total density. (b) From MP2 spin density.

Conclusions

In this study, a novel linear radical molecule XNgBCH$^-$ was investigated. It does not contain any fluorine atoms and contains a sulfur atom. The results show that XArBCH$^-$ is more stable than FArBCH. The energy required for the dissociation of XNgBCH$^-$ (X= O, S and Ng= Ar–Xe) is high enough to not easily dissociate (>10 kcal mol^{-1}). So we predict that these radical anions may be experimentally observable at low temperature.

References

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