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Borabenzene and Pentafluoroborabenzene Adducts with Dinitrogen, Xenon and Krypton: A Quantum–Chemical Study

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Abstract — Structural parameters of borabenzene and pentafluoroborabenzene molecules and their adducts with N_2, Xe, and Kr are calculated by the B3LYP quantum-chemical method. The adducts $C_6F_5B \cdot (N_2$, Xe, Kr) are characterized by the formation energies 36, 26, and 8 kcal mol^{-1}, bond lengths 1.45, 2.23, and 2.21 Å, charges +0.2 (N_2), +0.4 (Xe), and +0.3 au (Kr), and dipole moments 2.8, 7.0, and 6.0 D, respectively. The adducts $C_6H_5B \cdot (N_2$, Xe) have the total energies 18 and 11 kcal mol^{-1}, bond lengths 1.48 and 2.45 Å, charges +0.1 (N_2) and +0.3 au (Xe), and dipole moments 0.8 and 4.0 D, respectively. Unsubstituted borabenzene does not form a chemical bond with krypton.
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In this work we have performed a quantum–chemical study of borabenzene (**I**) and pentafluoroborabenzene (**II**) adducts with the xenon and krypton atoms and the dinitrogen molecule (Fig. 1). The equilibrium bond lengths, bond angles, formation energies, wave numbers of normal modes, and dipole moments of free molecules are calculated by the B3LYP/[C, B, Kr 6-311+G(3df); F, N, H 6-311++ G(d,p); Xe MIDI(3d)] method using GAUSSIAN [1].

The equilibrium configurations belong to the C_{2v} symmetry group, as evidenced by the absence of imaginary wave numbers in the vibration spectra and the location of all atomic nuclei in the *xy* plane. The atomic charges were found by differentiating the dipole moment with respect to z_A coordinates of atomic nuclei along the normal to the *xy* symmetry plane [2]. The sum Σ of the products of such charges $q_A^{\perp}$ and the vector radii of atomic nuclei $\mathbf{r}_A$:

$$\mu = \Sigma_A q_A^{\perp} \mathbf{r}_A$$

coincides with the mathematical expectation of the molecular dipole moment calculated by the formula:

$$\mu = \int[\Sigma_A Z_A \delta(\mathbf{r} - \mathbf{r}_A) - \mathbf{r}]\rho(\mathbf{r})dv,$$

where Z_A is the charge of atomic nucleus and $\rho(\mathbf{r})$, electron density (au) [2].

The high dipole moments of the adducts are explained by the high polarity of the electron–acceptor molecules **I** or **II** and high electrical charges of chemically bound inert gases. Dinitrogen is a very weak donor for electron acceptors **I** and **II**. Nevertheless, the strength of bonding is relatively high and the influence of the aromatic borazole ring on the boron–carbon and carbon–carbon bond length is stronger than in the xenon and krypton adducts. On coordination of N_2 the boron–carbon bond elongates by 0.05 Å and the adjacent carbon–carbon bond shortens by 0.02 Å. The elongation of the N–N bond is no more than 0.02 Å (Figs. 1 and 2). The B–N bond length calculated by us is 0.11 Å smaller than the value obtained earlier by the RHF/6-31G* method [4]. The B–Xe bond in adduct **II** · Xe is as little as 0.01 Å longer than the experimental C–Xe bond in pentafluorophenylxenon pentafluorobenzoate [3].

Among the adducts studied, **I** · Kr was found to be the only unstable van der Waals complex with the B···Xe distance of 3.2 Å. In the other adducts, the energies of bonds between molecular components are as follows, kcal mol^{-1} : **I** · NN 18, **I** · Xe 11, **II** · NN 36, **II** · Xe 26, and **II** · Kr 8. Our calculated bond energy in **I** · NN is 2 kcal mol^{-1} larger than that calculated in [4] by the MP2//RHF/6-31G* method.

The calculated vibration spectrum of the **I** · NN adduct is consistent with experimental [5]. Both contain a strong band that corresponds to stretching vibrations of the diazo group. The isotope substitution $^{14}N_2 \rightarrow {}^{15}N_2$ decreases the wave number and integral intensity of this vibration. The isotope splitting cal-

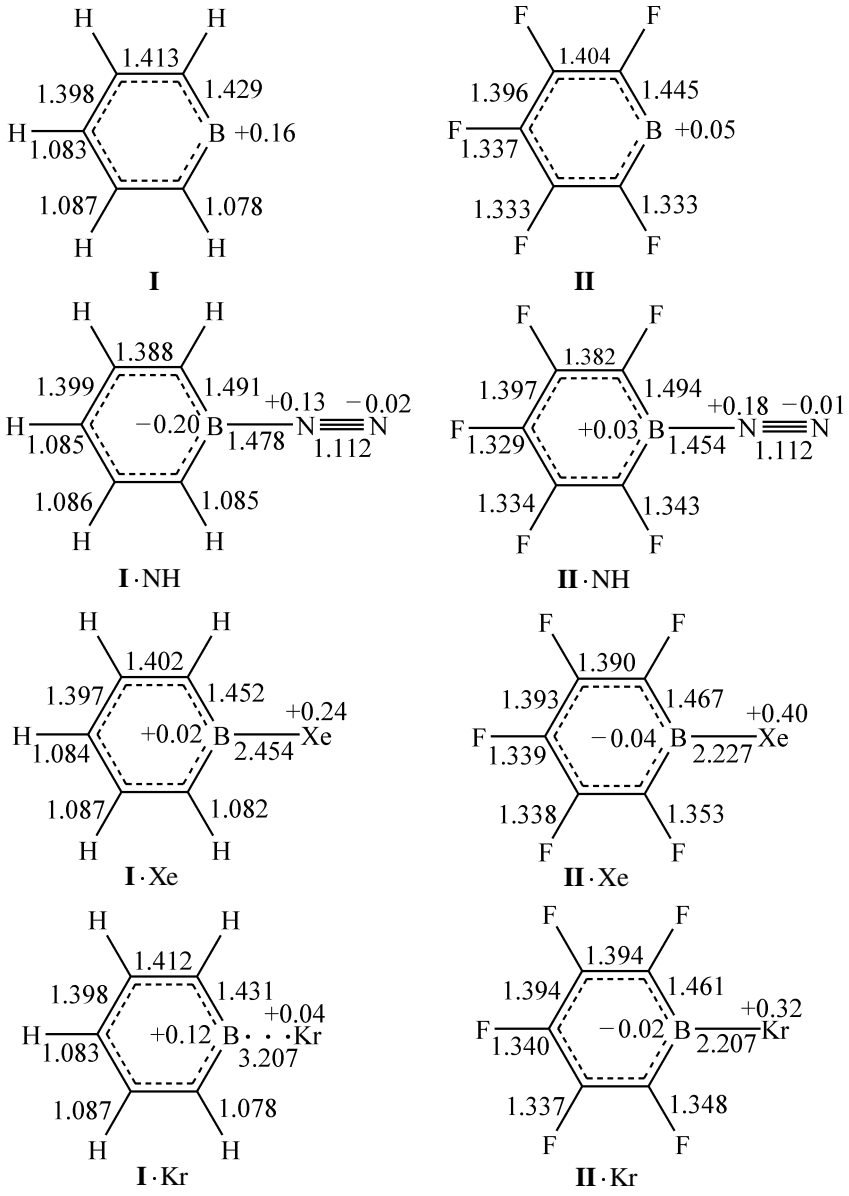

Fig. 1. Equilibrium internuclear distance (Å) and atomic charge (signed values, au) in the molecules of borabenzene (**I**), pentafluorobenzene (**II**) and their inert gas adducts.

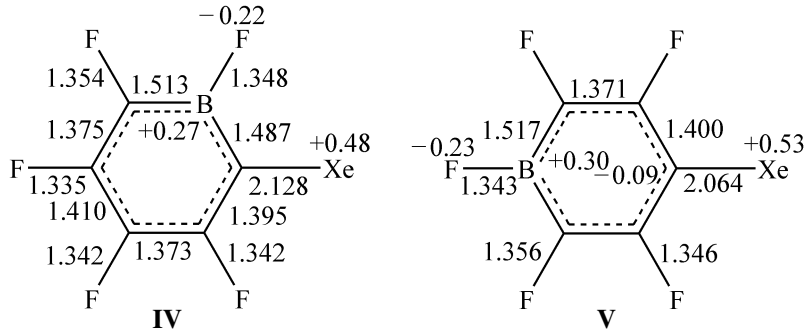

Fig. 2. Equilibrium internuclear distance (Å) and atomic charge (signed values, au) in the xenoneorganic molecules **IV** and **V** formed at β-decay of ^{11}C atom in the pentafluorophenylxenonium cation.

culated without account for best-fit data is 77 cm^{-1} (2262 $\rightarrow$ 2185 cm^{-1}) which is close to the experimental value 74 cm^{-1} (2198 $\rightarrow$ 2124 cm^{-1}) [5].

The total molecular energy of pentafluoroborabenzene (**II**) is 36 kcal mol^{-1} higher than the respective value for free diradical **III** derived from **II** by fluorine transfer from C^2 to B^1. However, the energy barrier to the isomerization **II** + 36 kcal mol^{-1} $\rightarrow$ **III** + 72 kcal mol^{-1} suggests that metastable molecule **II** may live long enough to react with inert gas. The same barrier prevents displacement of krypton from the **II**·Kr adduct by the neighboring fluorine atom: **II**·Kr + 36 kcal mol^{-1} $\rightarrow$ **III**·Kr + 64 kcal mol^{-1}. For the **II**·Xe adduct, the barrier of fluorine substitution for xenon is 56 kcal mol^{-1}, which is 30 kcal mol^{-1} above the energy of direct boron–xenon bond cleavage.

The calculated structural and energetic characteristics of the hypothetical metastable adducts allow us to expect that such adducts can be obtained and spectrally identified at low temperatures. The methods of synthesis of borabenzene derivatives have been described [5, 6]. The pentafluoroborabenzene **II**·Xe adduct may form together with its organoxenon isomers **IV** and **V** shown in Fig. 2 from the (pentafluorophenyl)xenonium cation [7] enriched with the radioactive ^{11}C isotope, as a result of $^{11}C \rightarrow {}^{11}B$ decay.

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