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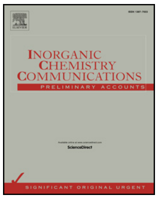

Short communication

Strong anion receptors based on antiaromaticity/aromaticity switching

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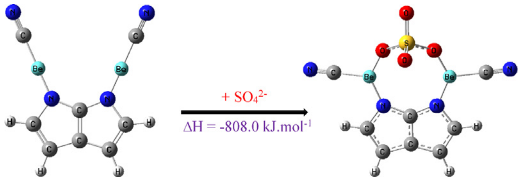
GRAPHICAL ABSTRACT



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ABSTRACT

A new class of anion receptors was designed using *N*-boryl and *N*-beryllium pyrrole derivative and their anion affinities were assessed in gas phase. The mechanism of these anion receptors is basis on aromatization of the pyrrole ring upon interaction with an anion. The anion affinities of these compounds toward F^-, Cl^-, NO_3^-, and SO_4^{2-} anions, computed at the B3LYP/6-311++G(d,p) level of theory, were in the range of 100–808 $kJ \cdot mol^{-1}$ indicating that these compounds are among the strongest anion receptors reported so far. Also, the anion receptors exhibit exceptional affinity toward SO_4^{2-} so that they can be considered as selective SO_4^{2-} receptors.

Anion receptors are of interest because of their applications in chemistry, biology and environmental sciences [1,2]. Therefore, considerable efforts have been devoted to design, synthesis and assessment of different types of the anion receptors. Recently, the researchers have focused on the design and synthesis of neutral receptors that interact with the anions, selectively [3–5]. The function of many of the anion receptors is mainly based on non-covalent interactions such as hydrogen bonding interactions [6,7]; therefore, the interaction between the receptor and the anion is usually weak. However, some anion receptors with higher binding energies have also been proposed [8,9].

Boron is known as a strong Lewis acid due to its empty p orbital, hence, many boron-based anion receptors have been reported [10]. To enhance the anion affinity of these anion receptors, the bidentate diboranes have also been proposed [11,12]. Another strategy is substitution of electron withdrawing groups to the boron-based anion receptors. Tris(perfluorophenyl)borane is one of the strongest boron-based anion receptors with F^- affinity of 406 kJ/mol [13].

The compounds containing beryllium act as strong Lewis acids because of electron deficiency of the Be atom [14]. Interactions of X-Be-Y compounds with different Lewis bases have been studied by Yanez and co-workers [15], extensively. Recently, they proposed a class of extremely strong bidentate Be-based anion receptors with anion (F^-, Cl^-, Br^-, NO_3^-, CN^-, SO_4^{2-}) affinities between 230 and 770 kJ/mol [16].

In this work, we use *N*-boryl and *N*-beryllium pyrrole derivatives to design a new type of anion receptors. The mechanism of these anion receptors is based on formation of an aromatic compound after interaction of the anions with the boron and beryllium atoms.

Structures of the molecules, anions, and complexes were fully optimized employing B3LYP functional and 6-311++G(d,p) basis set in gas phase. The frequency calculations were performed at 298.15 K at the same level of theory to obtain the enthalpies and Gibbs free energies of the interactions. Nuclear-independent chemical shift (NICS) parameter [17], as an index of aromaticity, was computed using the gauge-independent atomic orbital (GIAO) [18] method at the same level of theory. Isotropic, $NICS_{iso}$, and out-of-plane components, $NICS_{zz}$, of the chemical shift tensor were used as aromaticity indices. The NICS values at the ring surface, NICS(0), and at 1 Å above the ring, NICS(1), were also calculated using the Bq dummy atom as a probe [19]. All

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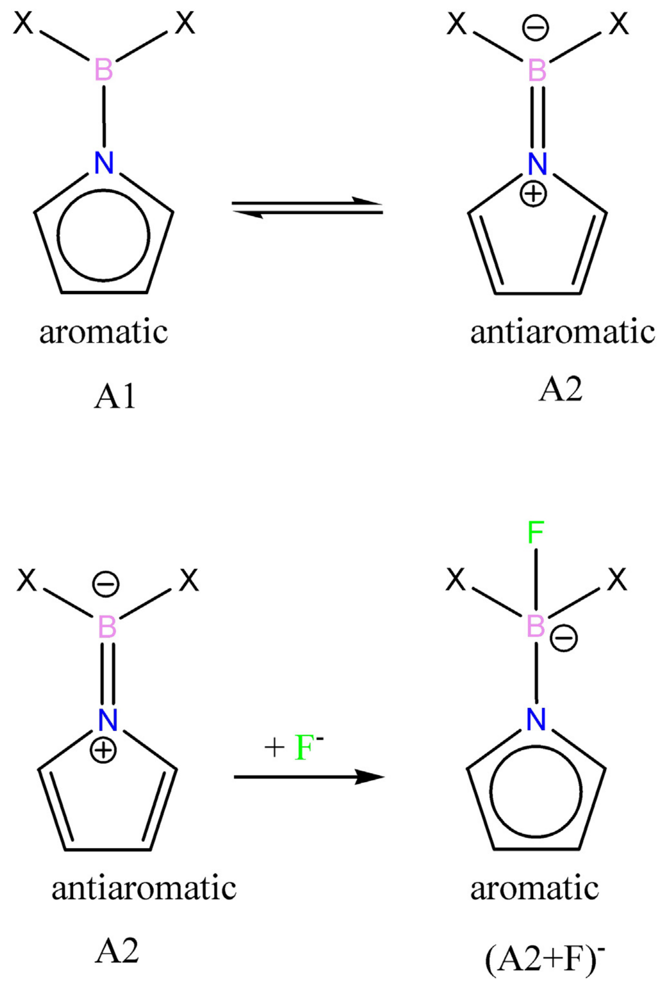

Fig. 1. *N*-boryl pyrrole derivatives have two resonance isomers A1 and A2. The antiaromatic zwitterion A2 is stabilized by electron withdrawing groups, X. After interaction of the isomer A2 with an anion, its antiaromatic ring obtains its aromaticity again.

calculations were carried out using Gaussian 09 software [20].

According to the Hückel theory of aromaticity, the monocyclic compounds with 4n + 2 π-electrons are aromatic [21]. Pyrrole, C_4H_5N, is an aromatic molecule because the lone pair on the nitrogen atom and four 2p electrons of carbons make an aromatic ring with 6 π-electrons. Fig. 1 shows an *N*-boryl pyrrole compound which has two resonance structures. The structure A1 has an aromatic ring in which the lone pair on the N atom participates in the electron delocalization of the 5-membered ring. Boron is an atom with electron deficiency, therefore, it may withdraw the lone pair electrons of the nitrogen to form an anti-aromatic zwitterion isomer, A2. Relative abundance of the isomers A1 and A2 can be controlled by inclusion electron withdrawing (EWG) and electron donating groups (EDG) instead of X. It is expected that the EWGs promote formation of the zwitterion A2 and increase its relative abundance. When the *N*-boryl pyrrole derivatives interact with an anion via their boron atom, the entering anion compensates the electron deficiency of the boron atom. Therefore, in the produced anion complex, the boron atom no longer need the lone pair electrons of the N atom and allows them to go and participate in the aromaticity of the 5-membered ring (Fig. 1). The same discussion is applicable about *N*-beryllium pyrroles.

Fig. 2 shows the optimized structures of the *N*-boryl and *N*-beryllium derivatives of pyrrole and their adducts with anion F^-. The aromaticities of these compounds are compared in Fig. 2 using NICS$(1)_{zz}$ index. Other NICS values including NICS$(0)_{iso}$, NICS$(0)_{zz}$, and NICS$(1)_{iso}$ are summarized in Table S1 (Supplementary materials). The molecules with more negative NICS values are more aromatic. The *N*-beryllium pyrroles are generally more aromatic than the corresponding *N*-boryl pyrroles; therefore, it can be concluded that the ability of boron to withdraw the electron pair of the nitrogen atom is more than that of beryllium. The compounds with the strong electron withdrawing group CN are less aromatic than those with X = H, F. In other words, CN substituent intensifies the electron deficiency of B and Be and facilitates formation of the antiaromatic zwitterionic isomer. Comparison of the NICS$(1)_{zz}$ values of the anion receptors and their corresponding adducts with F^- shows that the latters are more aromatic. In addition, the N—B and N—Be bond lengths in the neutral anion receptors are significantly shorter than those in the anionic adducts. Comparison of the aromaticities and the bond lengths confirms that boron and beryllium act as

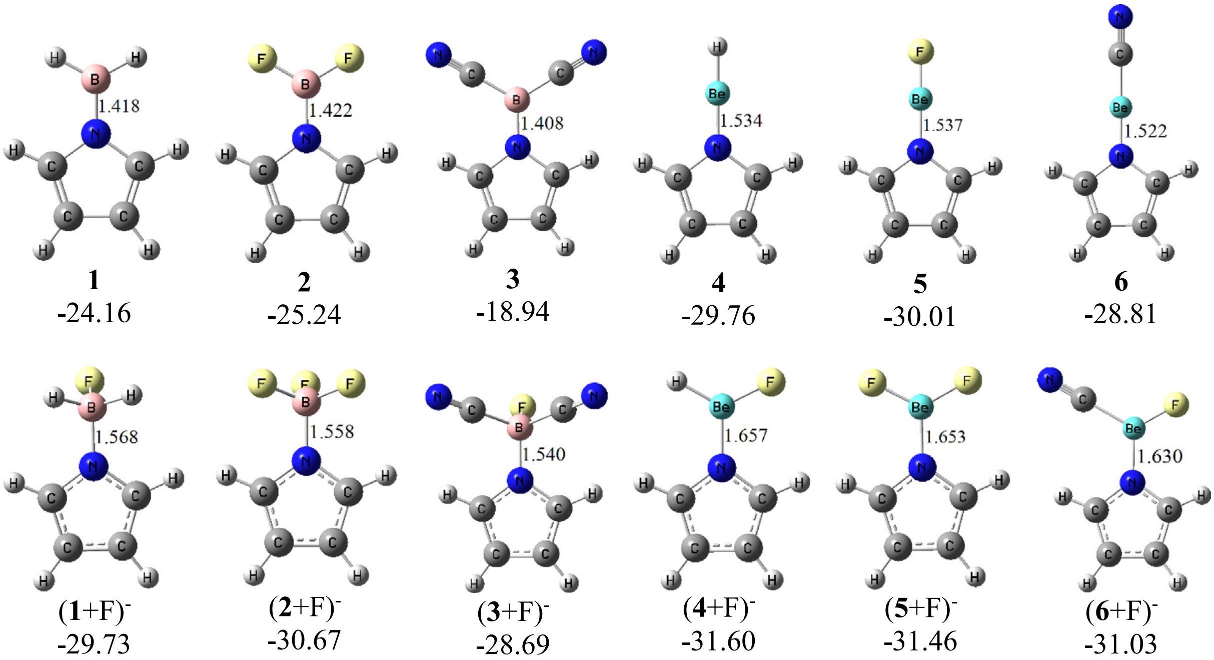

Fig. 2. The optimized strictures of the proposed anion receptors and their adducts with anion F^-. The negative values beneath the structures are the NICS$(1)_{zz}$ indices. The NICS$(1)_{zz}$ values and the bond lengths are in ppm and angstrom (Å), respectively.