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Research paper

# Functionalization of benzene by superhalogens

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ABSTRACT

We perform *ab initio* MP2/6-311++G(d,p) calculations to analyze the molecular properties and aromaticity of $NO_3$, $BO_2$ as well as $BF_4$ superhalogen substituted benzene and compare them with well known electron withdrawing group substituted benzene such as $C_6H_5F$ and $C_6H_5CN$ in neutral and ionic forms. It has been noticed that the properties (including aromaticity) of $C_6H_5BO_2$ closely resemble those of $C_6H_5F$ and $C_6H_5CN$. On the contrary, $C_6H_5NO_3$ possesses some quite different properties such as high electron affinity, small frontier orbital energy gap and enhanced aromaticity. It is also revealed that $C_6H_5BF_4$ exists only in the form of $C_6H_5F\cdots BF_3$ complex.

## 1. Introduction

Benzene ring is significantly stabilized due to complete delocalization (resonance) of $\pi$-electrons, which reduces its reactivity toward addition reactions. Note that benzene possesses high ionization energy (IE) and no positive electron affinity (EA). This is why whole chemistry of benzene is based on electrophilic substitution reactions. These substitution reactions are greatly influenced by the functional groups attached to the ring. The electron-withdrawing (EW) functional groups such as —F, —CN, —$NO_2$, —$CF_3$, etc. are known as ring deactivating since they pull electrons from the ring and deactivate it, i.e., make the reaction slower. Many studies [1–3] suggest that a group substituting a hydrogen atom of benzene affect only weakly the $\pi$-electron delocalization in the ring. This reflects the tendency of aromatic systems to retain their initial $\pi$-electron structure during the reaction course, leading to aromatic substitution. However, it has been noticed [3] that the substitution by EW groups increases the ionization energy and dipole moment of the ring. This effect becomes more pronounced with strong EW groups. The —F and —CN are stronger EW substituents due to their high EA. There are some species possessing higher EA than Cl, which are referred to as superhalogens.

The concept of superhalogen was proposed by Gutsev and Boldyrev in 1981 [4], and experimentally verified by Wang et al. in 1999 [5]. Superhalogens have been subject of frequent investigations in the last three decades [6–12]. Owing to their large EA, superhalogens possess capability to oxidize both Xe atom and $O_2$ molecule simultaneously [13] as well as ionize benzene ring [14]. Recently, it has been noticed [15,16] that the protonation of superhalogen anions leads to superacids, which are more acidic than pure sulphuric acid, the strongest mineral acid. Superhalogens have been employed as building block of new electrolytic salts for lithium ion batteries [17,18] as well as new materials for hydrogen storage [19]. The study of superhalogen is an increasingly interesting as well as rapidly growing area of research. In this letter, we discuss the substitution of superhalogens on benzene and compare with those of strong EW group substituted rings. We have chosen $BO_2$, $NO_3$ and $BF_4$ superhalogens as substituent, and compare them with F and CN group substituent.

## 2. Computational details

All functionalized benzene, $C_6H_5X$ (X = F, CN, $NO_3$, $BO_2$ and $BF_4$) were studied using the second order Møller-Plesset perturbative (MP2) approach [20] and 6-311++G(d,p) basis set in Gaussian 09 program [21]. The total energy and geometry have been obtained without any symmetry constraints in the potential energy surface. The vibrational analysis has been performed to ensure that all structures belong to true minima. The (adiabatic) EA of X has been calculated by the difference of the total electronic energy of X and its anion ($X^-$) at their equilibrium geometries. The aromaticity of ring has been analyzed by harmonic oscillator model of aromaticity (HOMA) index [22,23] and nucleus independent chemical shift (NICS) [24,25] value. NICS is computed at the centre of ring plane using gauge independent atomic orbital (GIAO) approach. The HOMA index for six-membered ring is computed by:

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$$\mathrm{HOMA} = 1 - (\alpha/6)\sum (R_{\mathrm{opt}} - R_{\mathrm{i}})^2$$

where $\alpha$ is an empirical constant such that HOMA = 0 for non-aromatic systems and HOMA = 1 for aromatic system with all bond lengths ($R_i$) of the ring equal to the optimal value ($R_{opt}$) as reported [22,23].

## 3. Results and discussion

We start our discussion considering the electron-withdrawing groups. F and CN both need exactly one electron to complete their octet, consequently, they possess large EA values. From Table 1, the adiabatic EA of CN is found to be even larger than F. This is only group whose EA exceeds that of F and therefore, it is also referred to as pseudohalogen group or halogenoid [26,27]. Like F and CN, superhalogens also require one electron to be stabilized. The equilibrium structures of $NO_3$, $BO_2$ and $BF_4$ anions are displayed in Fig. 1. The adiabatic EAs of $NO_3$, $BO_2$ and $BF_4$ along with corresponding experimental values are also listed in Table 1. Since precise EA calculation is not our objective, it should be noted that our calculated electron affinities of F and $NO_3$ are underestimated whereas those of CN and $BO_2$ are overestimated when compared with their latest experimental values available [28–31] (see Table 1). Therefore, $NO_3$, $BO_2$ and $BF_4$ possess fairly large EA and behave as superhalogens.

Now we discuss the properties of F and CN substituted $C_6H_6$. The optimized structures of $C_6H_5F$ and $C_6H_5CN$ as well as their anions and cations are displayed in Fig. 2. These structures are planar in which the bond length $C_6H_5$—X (X = F) is found to be 1.352 Å, which is equal to its anion but reduced to 1.313 Å for cation. This trend is slightly different for X = CN in which the bond length $C_6H_5$—X (1.437 Å) is reduced to 1.419 Å in both anion and cation. The ring bond lengths for $C_6H_5F$ are found in the range 1.392–1.400 Å (neutral), 1.391–1.401 Å (anion), 1.354–1.449 Å (cation). For $C_6H_5CN$, the bond lengths range become 1.397–1.406 Å (neutral), 1.358–1.433 Å (anion) and 1.378–1.438 Å (cation). The adiabatic IE and EA of $C_6H_5X$ are listed in Table 2. Our calculated IE values of $C_6H_5F$ (9.41 eV) and $C_6H_5CN$ (10.29 eV) slightly overestimate corresponding experimental values, 9.35 eV [32] and 10.13 eV [33]. The IE and EA values of $C_6H_5CN$ are only slightly larger than that of $C_6H_5F$. The energy gap ($E_{gap}$) between HOMO and LUMO is an important parameter to analyze chemical reactivity of molecules. According to Pearson [34], molecules with larger $E_{gap}$ values are chemically more hard and hence, less polarizable. $C_6H_5CN$ possesses larger $E_{gap}$ value than $C_6H_5F$, although difference is only 0.2 eV. Interestingly, the dipole moment ($\mu$) of $C_6H_5CN$ (5.08 D) is much larger than that of $C_6H_5F$ (1.97 D). This suggests that $C_6H_5CN$ is highly polar molecule. The aromaticity of $C_6H_5X$ is quantified by HOMA indices and NICS values, also listed in Table 2. HOMA index provides a structural measure of aromaticity, which reflects the bond length equalization within the ring. The NICS is an indirect but the most popular measure of aromaticity, which takes ring currents into account. The systems with more negative NICS values are more aromatic and vice versa. We have listed NICS (which is contributed by sigma and pi electrons) and its z-component ($NICS_{zz}$, which is mainly contributed by pi electrons) at the ring centre. Note that the HOMA and NICS values suggest that $C_6H_5F$ is more aromatic than $C_6H_5CN$, mainly due to contribution of pi electrons. Below we discuss the $NO_3$, $BO_2$ and $BF_4$ superhalogen monosubstituted benzene.

**Table 1**
Adiabatic electron affinity (EA) of various substituents along with superhalogens.

| Group | Calculated EA | Experimental | |
|---|---|---|---|
| | (eV) | EA (eV) | Ref. |
| F | 3.24 | 3.40 | 28 |
| CN | 4.48 | 3.86 | 29 |
| $NO_3$ | 3.45 | 3.94 | 30 |
| $BO_2$ | 4.97 | 4.46 | 31 |
| $BF_4$ | 6.73 | - | – |

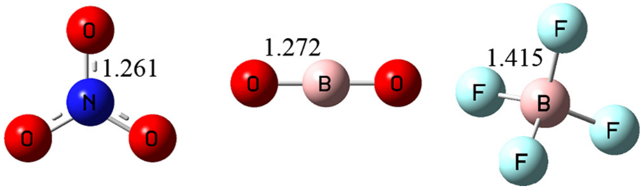

**Fig. 1.** The equilibrium structures of $NO_3$, $BO_2$ and $BF_4$ superhalogen anions.

### 3.1. $NO_3$. substituted benzene ($C_6H_5NO_3$)

The equilibrium structures of $C_6H_5NO_3$ with its anion and cation are displayed in Fig. 3, with $C_6H_5$—$NO_3$ bond length of 1.479 Å (neutral), 1.495 Å (anion) and 1.486 Å (cation). Like $C_6H_5F$ and $C_6H_5CN$, the rings are planar with bond lengths of 1.393–1.400 Å (neutral), 1.394–1.402 Å (anion) and 1.380–1.453 Å (cation). Both IE and EA values of $C_6H_5NO_3$ are larger than those of $C_6H_5F$ and $C_6H_5CN$. This may suggest that $C_6H_5NO_3$ is much reactive with the tendency to accept the electrons. This increased reactivity of $C_6H_5NO_3$ is also reflected in its smaller $E_{gap}$ value (almost half of $C_6H_5CN$). Like $C_6H_5CN$, however, $C_6H_5NO_3$ is polar due to large $\mu$ value (4.72 D), unlike $C_6H_5F$. Even more interesting are HOMA and NICS values. For instance, HOMA value of $C_6H_5NO_3$ (0.98) is larger than those of $C_6H_5CN$ (0.95) and $C_6H_5F$ (0.97) which suggests that $C_6H_5NO_3$ is more aromatic than $C_6H_5CN$ and $C_6H_5F$. This is also supported by their NICS and $NICS_{zz}$ values. The enhanced aromaticity of $C_6H_5NO_3$ is mainly due to pi electrons.

### 3.2. $BO_2$. substituted benzene ($C_6H_5BO_2$)

Fig. 3 also displays the optimized structures of $C_6H_5BO_2$ as well as its anion and cation such that the $C_6H_5$-$BO_2$ bond length is 1.399 Å (neutral), 1.355 Å (anion) and 1.345 Å (cation). Like $C_6H_5F$, $C_6H_5CN$ and $C_6H_5NO_3$, neutral and cationic $C_6H_5BO_2$ structures possesses the planar ring, with the bond lengths of 1.394–1.400 Å and 1.397–1.411 Å, respectively, but the ring is distorted from planarity by around 50° degree in anion. The IE of $C_6H_5BO_2$ is comparable to that of $C_6H_5F$ but EA is slightly larger than that of $C_6H_5CN$. Its $E_{gap}$ is comparable to that of $C_6H_5CN$ (slightly larger than that of $C_6H_5F$). Furthermore, the $\mu$ value of $C_6H_5BO_2$ (4.87 D) is also comparable to that of $C_6H_5CN$ (much larger than that of $C_6H_5F$). Even more interesting are HOMA and NICS values. For instance, HOMA value of $C_6H_5NO_3$ (0.98) is larger than those of $C_6H_5CN$ (0.95) and $C_6H_5F$ (0.97) which suggests that $C_6H_5NO_3$ is more aromatic than $C_6H_5CN$ and $C_6H_5F$. This may suggest that the molecular properties of $C_6H_5BO_2$ closely resemble those of $C_6H_5CN$. However, HOMA and NICS values reveal that the aromaticity of $C_6H_5BO_2$ range between those of $C_6H_5F$ and $C_6H_5CN$.

### 3.3. $BF_4$. substituted benzene ($C_6H_5BF_4$)

$BF_4$ belongs to a rich class of superhalogen, as most of the superhalogens employ F ligands [6–12]. The optimized structures of $C_6H_5BF_4$ along with their anion and cation are displayed in Fig. 4. One can note that the neutral and cationic $C_6H_5BF_4$ resemble the structure of $C_6H_5F\cdots BF_3$ complex with the bond distance of 2.461 Å and 3.408 Å, respectively. In anion, we notice that $BF_4$ dissociates into F and $BF_3$ fragments which interact separately with the ring system (see Fig. 4). The $C_6H_5$—F bond length in $C_6H_5BF_4$